# VACUUM POLAROGRAPHIC INVESTIGATION
# OF AIR OXYGEN DISSOLVED
# IN ETHYLENE GLYCOL

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An all-glass polarographic cell for studies under reduced pressures (from $10^1$ to $10^{-1}$ Torr) was constructed for investigations of de-aeration of ethylene glycol by evacuation in dependence on temperature (20—70°C). The removal of oxygen by a stream of nitrogen was studied in the usual polarographic cell. Both procedures, a combination of which is used in vacuum distillations of liquids, are different in their efficiency in favour of bubbling by inert gas, however, at normal pressure. Rise of temperature increased the efficiency of both methods. In the case of suspensions of solid diammonium terephthalate in ethylene glycol both methods were practically equivalent, in the case of terephthalic acid all the oxygen dissolved could not be removed even after several hours. From the dependence of the product $i_d \sqrt{\eta}$ on the composition of the water–ethylene glycol mixtures (0—100 vol. %) it was concluded that air oxygen is more soluble in ethylene glycol than in water (approximately $10^{-3}$ mol/l at room temperature).

Up to this time, little interest has been shown for polarography in practically non-aqueous ethylene glycol (EG)[1-5]. As to the air oxygen dissolved in EG according to Henry's law, it was only stated[1] that it gives a double wave similar to that obtained in aqueous solutions. As attention was mostly directed towards polarographic studies of inorganic cations in which oxygen badly interferes, much effort was spent to its removal. In the case of dry, oxygen-free hydrogen, it has been found necessary to gas the solution for two hours[1], in the case of nitrogen of the same quality the time has not been stated[2], being probably 5—10 minutes. There is no study concerning the character of oxygen reduction on dropping mercury electrode in the case of EG. As to the solubility of air oxygen in non-aqueous organic solvents, it has been only generally noted that in many cases it is greater than in water[6,7].

The aim of this work was to obtain semi-quantitative data on air oxygen in EG compared to water and further to investigate the behaviour of oxygen in suspensions of solids in EG and the influence of temperature.

## EXPERIMENTAL

### Chemicals

Ethylene glycol was a commercial product (Slovnaft, Bratislava). Its physical constants and infrared spectrum were identical with the published ones. Purity of EG was moreover checked by gas–liquid chromatography, polarography, UV and atomic absorption spectrometry. According to chromatographic analysis our EG contained $0.03-0.05$ w. % of diethylene glycol, according to polarographic analysis[8-10] the sample did not contain detectable traces of aldehydic compounds, according to its UV-spectrum (1 cm cell) it contained a compound characterized by maximal absorption at 203·5 mμ (presumably glycolic acid -- about $10^{-3}$ M). The content of iron, nickel, and chromium was less than 0·5 p.p.m. for each element, the content of sodium was 0·25 p.p.m., potassium was not detected. The content of water (K. Fischer method) was 0·3 w. %, *i.e.* it represented about $0.2$M-$H_2O$ in EG. During half a year of storage, the stock sample did not change its UV-spectrum and water content.

LiCl and KCl were used as supporting electrolytes for polarographic measurements. Neither of the chlorides contained polarographically active impurities, before use they were finely divided, dried at 120°C, and stored in a desiccator.

Fuchsine (Fluka AG, Basel, Switzerland), terephthalic acid (Mobil, USA), and diammonium terephthalate (a laboratory sample) were used directly.

### Instruments

The cell for polarography at reduced pressures, constructed in this laboratory, is schematically shown in Fig. 1. The water jacket and thermostat made it possible to control temperature within ±0·5°C. The mercury pool was used as a reference electrode.

The polarographic capillary was drawn from a thick wall tube (Sial) with internal diameter 1 mm. The obtained capillary was conical, its orifice having the diameter about 0·08 mm. The other end of capillary was sealed to a glass tube (passing through the cap of the cell) on which a transparent, thick wall (2 mm) plastic tubing* was put on, connections were cemented with Apiezon Wax W 40. Electrical contact between the mercury in the reservoir and the mercury in the side arm below the reservoir was arranged by a sealed-in platinum wire. The spherical reservoir was topped with a ground, vacuum male joint. The polarographic cell and the reservoir were connected by vacuum rubber tubings through a McLeod manometer and a cooling trap (filled with glass balls and immersed into liquid nitrogen) to a one-stage oil pump (output about 1 m³/h). The vacuum stopcocks were placed between the pump and the reservoir and/or the cell. All stopcocks and ground joints were greased with Dow Corning High Vacuum Silicone Grease.

An important feature of the polarographic cell is the distance between the mercury pool surface (at the beginning of a measurement) and the capillary tip. During measurements under reduced pressure it is not possible to remove mercury from the cell and therefore the rate of growth of mercury level predetermines the longest time of such a polarographic measurement. Furthermore, the measurement of diffusion currents under reduced pressure is unfavourably influenced by evolution of bulky gas bubbles in the analyzed solution because they stir it and accelerate its degassing and, moreover, they interfere with dropping of mercury. This above all may be caused by air which can stick between the mercury pool and the cell wall. It can be prevented by a careful

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*      During an evacuation of the cell and of the reservoir de-gassing of mercury in the tubing proceeds so that the mercury column can be disrupted by a bubble of air.

preparation of the cell for the measurement. During measurements under elevated temperatures another source of bulky bubbles can be a greater amount of water in EG which distils under reduced pressure from such a solution. This phenomenon was not observed when the concentration of water was less than 0·5M, *i.e.* that any contact of the analyzed EG with moist air must be prevented. Furthermore, after every gassing of the analyzed solution with dry gas it is necessary to wait some time till all visible gas bubbles liberate from the solution and the capillary tip. This eliminates the third possible source of bulky bubbles. The evolution of small bubbles in the solutions in later stages of evacuation has no remarkable effect on the reproducibility of the measurements of limiting current.

Polarographic measurements were carried out with the aid of a commercial polarograph, type LP-60 (Laboratory Instruments, Prague), viscosities were measured on Ubbelohde U-2 and U-3 viscometers at $25.0°C$, electrical conductivity was determined by means of a conductometer OK-102 with the frequency of 3 kHz (Radelkis, Hungary), for pH measurements the instrument Polymetron 42 D (Glattbrugg, Switzerland) was used.

Procedures

All polarographically analyzed solutions in which dissolved air oxygen was to be determined were gassed for 5 minutes by dry air or nitrogen at a given temperature prior the measurement. Recordings of the heights of both oxygen waves or of the residual current were reproducible with an accuracy of $\pm 2\%$. Fuchsine was used for suppression of the oxygen maximum (stock solution in EG was 0·1 w. %) with the final concentration of $1 . 10^{-3}$ w.% in each analyzed solution at 25°C. The efficiency of maximum suppression decreased with increasing temperature, however, further increase of fuchsine concentration led to an interfering wave, presumably of fuchsine. For this reason, the above mentioned final concentration of fuchsine was used at all temperatures.
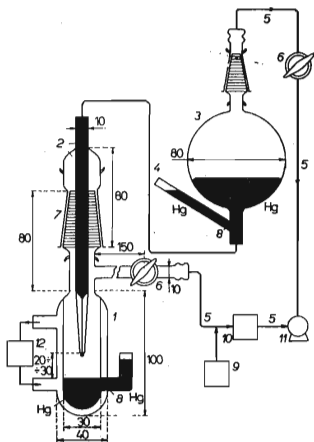


Fig. 1

The Scheme of Cell, Capillary, and Reservoir for Polarography at Reduced Pressures

*1* Cell with water jacket, *2* capillary with the cap of the cell, *3* mercury reservoir, *4* flexible transparent vacuum plastic tubing, *5* vacuum rubber tubings, *6* single-way vacuum stopcocks with 8 mm bore, *7* vacuum ground joints 29 resp. 19 mm, *8* sealed-in platinum wires, *9* McLeod manometer, *10* cooling trap, *11* oil pump, *12* circulation thermostat.

The decrease of the air oxygen content in EG by evacuation in dependence on time was studied at a constant applied voltage of $-1.60$ V. The decrease of the limiting current, which is the sum of the first and the second oxygen wave, was corrected for the residual current value at the same potential. For time-saving reasons, the time necessary for only half decrease of the limiting current was measured. This value moreover offered the possibility to compare the results of evacuation of oxygen from EG at different temperatures as these variations cause changes of many factors simultaneously: viscosities of solutions, drop time, and probably also the solubility of oxygen in EG. Generally, the measurement under reduced pressure must begin with evacuation of the cell and then of the reservoir, otherwise the analyzed solution penetrates into the capillary and can cause its stuffing. At the end of measurement it is necessary to proceed in the reverse order.

The drop time at normal pressure differs from the value measured at reduced pressures by some per cents, if the height of mercury column is constant. For this reason, it is necessary to check visually any formation of bubbles in the tubing between the cell and the reservoir: during the measurements of polarographic curves this malfunction is immediately indicated by circuit break but under reduced pressure during the measurement of drop time when the circuit was disconnected on purpose, this can escape attention and lead to an erroneous observation.

## RESULTS

According to literature[1] it was observed that oxygen dissolved in EG gives two reduction waves. In the absence of surfactants, a pronounced sharp maximum of the first kind is observed on the first oxygen wave, its height depending on the concentration of the supporting electrolyte. With a set of solutions $1 \cdot \left(10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}\right)$M-KCl in EG the highest maximum was observed with $1 \cdot 10^{-3}$M-KCl, in agreement with the data for oxygen in water[11]. Instead of the proposed[3] ethylcelullose for suppression of oxygen maximum in EG, we successfully used fuchsine. The ratio of heights of both waves was $1 : 1$ without changing both halfwave potentials. The $0.1$M concentration of supporting electrolytes (KCl, LiCl) was chosen as optimum, to prevent the reaction of excess chloride ions with oxygen as it has been proposed for aqueous solutions[12]:

$$Hg + 2 Cl^- + O_2 + 2 H_2O = HgCl_2 + H_2O_2 + 2 OH^- . \qquad (1)$$
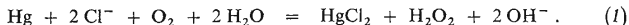
In the case of KOH as the supporting electrolyte ($0.1$M) an instantaneous, incomplete suppression of oxygen maximum occurred, the maximum being rounded. In the case of $0.1$M-LiClO$_4$ ($+$ fuchsine) a lowering of the second oxygen wave was observed so that the ratio of both waves was $0.85$. These two supporting electrolytes were not used in further measurements.

Electrical conductivity of the $0.1$M-LiCl solution in EG ($22°C$) was measured in the usual and the "vacuum" polarographic cell. It ranged during the formation of a mercury drop (open circuit value of drop time was $1.3$ s) between $50-200$ µS, $i.e.$ during the polarographic measurements (currents $1-5$ µA) the $iR$-drop amounted to $10-100$ mV (the sensitivities of the instrument were $1/10-1/50$).

As the aim of this work was not to determine the half-wave potentials of depolarizers in EG, we quote only the intervals of the half-wave potentials for both oxygen

waves (against mercury pool): from $-0.1$ to $-0.4$ V for the first wave and from $-0.9$ to $-1.3$ V for the second one.

De-aeration of solutions by inert gas proved that both waves belong to oxygen, the addition of $H_2O_2$ solution in water to the KCl solution in EG increased the second wave without changing its half-wave potential, *i.e.* the second wave corresponds to the electroreduction of hydrogen peroxide.

*Solubility of air oxygen in the water–EG mixtures.* A set of $0.1$M solutions of LiCl in the mixtures was prepared, changing the volume content of the components by 10% in the range $0-100$ (25°C). The value of the limiting current at $-1.60$ V was measured and corrected for the residual current. At the fuchsine concentration of $1 . 10^{-3}$ w. %, the height of each oxygen wave was determined by the rectangular method. Ratios of both heights were averaged for eleven solutions and gave the value $1.0 \pm 0.1$ (two measurements for each solution). The dependence of the height of the limiting current at $-1.60$ V on the composition of the water–EG mixtures in the presence of fuchsine was the same as in the absence of fuchsine (Fig. 2, curve *1*). According to the previous work[1], the product of the limiting current value and of the viscosity in equimolar solutions of thallium(I) ions in the water–EG mixtures is constant over the whole range of water concentrations. Therefore the values of kinematic viscosity of both series of $0.1$M-LiCl solutions were measured and mean values of the product $i_d/\eta$ were plotted against the composition of the mixtures (Fig. 2, curve 2). It may be seen that the solubility of air oxygen is not constant. To check the effect of our acidic maximum suppressor, the pH* values of both series of $0.1$M-LiCl solutions both with and without fuchsine were measured.*
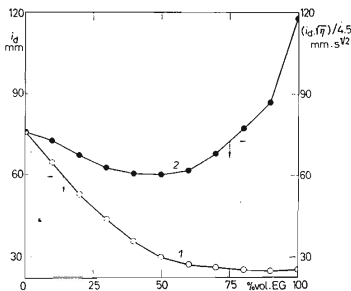


Fig. 2

The Dependence of the Oxygen Limiting Current $i_d$ *1* and of the Product $i_d \sqrt{\eta}$ 2 on the Composition of Water–EG mixtures

Measured in usual cell. *1* $0.1$M-LiCl with or without fuchsine $(1 . 10^{-3}$ w. %), at $-1.60$ V, sensitivity 1/50, $h = 71$ cm, $t(0 \text{ V}) = 2.01 \pm 0.07$ s, $t(-1.60 \text{ V}) = 1.40 \pm 0.04$ s, $25.0 \pm 0.5°$C; 2 viscosities $\eta$ were measured at 25.0°C, the $i_d \sqrt{\eta}$ values were divided by a factor 4.5 to normalize the second curve.

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* The pH* values used in this paper are readings of the pH-meter with a glass electrode, related to calibration of the instrument by means of aqueous buffer solutions (phthalate, pH 4; borate, pH 9).

*Removal of oxygen from EG by means of bubbling with nitrogen or by evacuation.*
As it was already stated, 3 – 10 minutes of lively bubbling with nitrogen are sufficient
in practice for removal of the dissolved oxygen from 0·1M-KCl solutions in EG at the
given sensitivity of the recorder. Repeated bubbling with dry air or with nitrogen
for 5 – 10 minutes gave reproducible recordings of the oxygen waves or of the residual
current. It has to be pointed out that both gases should be well dried with regard
to the hygroscopicity of EG[13] and to the thus caused viscosity changes of the solution
under investigation. Gassing of EG with pure oxygen led to an about fivefold increase
of the height values of both waves according to the change of oxygen partial pressure.

The dependence of the oxygen removal from EG by means of cell evacuation upon
time was investigated at several temperatures within the interval 20 – 80°C. Prior to
every measurement at a given temperature, the value of the residual current was
registered after saturation of the solution with nitrogen under normal pressure.
Then followed the saturation with dry air for 5 minutes at the same temperature
and evacuation after 15 minutes waiting. The dependence of the oxygen content
decrease at 21°C by means of the evacuation of EG upon time is seen in Fig. 3.
The heights of the limiting current at constant potential −1·60 V were measured
and corrected for the residual current. In determining the dependence of the oxygen
decrease on temperature, the periods necessary for half-diminution of this limiting
current were measured (Table I). It may be seen that the efficiency of the evacuation
increases with temperature increase.

*Removal of oxygen from suspensions of solids in EG.* The purpose of these experi-
ments was to verify whether the efficiency of gassing with nitrogen is the same when
solid materials are suspended in EG. Terephthalic acid (TH$_2$) and diammonium tere-
phthalate (TAm$_2$) were used. As the solubility of TH$_2$ in EG is very low, LiCl (0·1M)

TABLE I
The Dependence of the Evacuation Time[a] of Oxygen on Temperature

| Temperature, °C | 21[b] | 40·0 | 50·0 | 60·0 | 70·0 |
|---|---|---|---|---|---|
| Time, min | 340 – 360 | 88 | 58 | 25 | 19 |
| Drop time, s [c] | 1·29 | 1·06 | —[d] | 1·00 | 0·92 |
| Pressure, Torr [e] | 12 | 21 | 15 | 18 | 28 |
| EG, Torr [f] | $10^{-2}$ | $10^{-1}$ | 0·7 | 1·5 | 2·7 |
| Sensitivity | 1/10 | 1/15 | 1/15 | 1/20 | 1/20 |

[a] Time necessary for half-decrease of the limiting current at −1·60 V corrected for the residual
current value. For all measurements $h = 48·5$ cm, 0·1M-LiCl in EG (0·3 w.% of H$_2$O, 1.10$^{-3}$ w.%
of fuchsine); [b] accuracy ±1°C, otherwise ±0·5°C; [c] at −1·60 V; [d] not measured; [e] the lowest
pressure attained to usually at the end of measurement; [f] saturated vapor pressure of dry EG[28,29].

was used as the supporting electrolyte, whereas $TAm_2$ served alone for this purpose, its solubility in EG being approximately $0.1M$ at room temperature.

In the case of 10% suspension of $TAm_2$ in EG, gassing with nitrogen had the same effect on the oxygen removal as in the case of the saturated $TAm_2$ solution at 22°C, 5 minutes being sufficient for practical disappearance of both oxygen waves. The polarogram showed only one wave, probably corresponding to the terephthalate ion appearing at approximately $-1.65$ V, as it is also the case for aqueous solutions ($-1.65$ V vs S.C.E., ref.[14]). In the case of 10% suspension of $TH_2$ in $0.1M$-LiCl in EG at 25°C, a diminution of $15-20\%$ of oxygen waves took place after 5 minutes of gassing, but afterwards the decrease of oxygen slowed down very steeply and did not attain 50% during 1 hour. After 1 hour gassing at 80°C, the wave of hydrogen peroxide is likewise still observable.

The removal of oxygen from $TH_2$ suspension in EG by means of evacuation was investigated at 20°C and 80°C. As no mixing takes place during the evacuation, the suspension settles down during the measurement (the drop time is also not observable) and the results may be considered only as qualitative ones. At 80°C, a rather steep decrease of the heights of both oxygen waves followed after $5-10$ minutes, but very small waves were still observable even after 3 hours, namely the oxygen maximum upon the first wave. An addition of aqueous hydrogen peroxide to the suspension after finishing the measurement caused an increase of the second wave without changing its half-wave potential. This verified that the remaining second wave corresponds to the electroreduction of hydrogen peroxide.
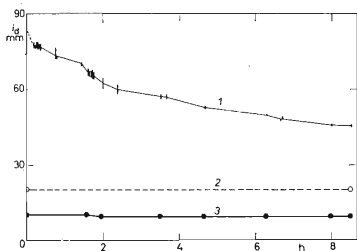


Fig. 3

The Dependence of the Limiting Current $i_d$ at $-1.60$ V on the Time of Evacuation of Oxygen from EG

1 $0.1M$-LiCl in EG ($0.3$ w.% of water, $1 . 10^{-3}$ w. % of fuchsine), sensitivity 1/10, $h = 48.5$ cm, $t(0 \text{ V}) = 1.36$ s, $21 \pm 1°C$; 2 value of the residual current at $-1.60$ V measured at pressure of 1 atm of nitrogen; 3 recorder zero.

DISCUSSION

As there are no available data concerning the nature of electroreduction of oxygen dissolved in EG, the following assumption has been implicitly made in this work: we deal here with oxygen electroreduction in the presence of water, contained in EG at low concentrations. This assumption does not contradict the experimental facts, namely that dissolved oxygen gives two reduction waves even in aprotic solvents like acetonitrile[15] or dimethyl sulphoxide[16]. Analytical data about the content of water in non-aqueous solvents used in polarography are either lacking or they prove that concentrations of present water does exceed by at least an order of magnitude the stoichiometric concentration of $O_2$. Such an excess of water substantiates the assumption[17,18] that the mechanism of the electroreduction is here similar to that in the system $O_2-H_2O$ when the concentration of dissolved oxygen under normal pressure and composition of air amounts[19] to $2-3 . 10^{-4}$ mol/l at $25.0°C$.

The proposed mechanisms of electroreduction of oxygen assume, however, that there is a dependence on concentration of hydrogen or hydroxide ions[17], i.e. determinations should be carried out in buffered solutions. It is known[20] for the $O_2-H_2O$ system that the ratio of both oxygen waves is equal to unity and, furthermore, the reversibility of the electroreduction of hydrogen peroxide to water is ensured in strongly alkaline media[17]. Irreversibility of this reaction in the case of non-aqueous solvents is believed to be the cause of the lowering of the second oxygen wave in comparison with the first wave[15–17,21]. In this work we dealt with measurements of solubility of oxygen in the water–EG mixtures, however, the solutions were not buffered due to evident reasons, in particular due to uncertainty in defining pH in the last sample with concentration of about 99.7 w.% of EG. In the case of 0·1M-LiCl we used fuchsine (hydrochloride of tris(aminophenyl) methane dye) as the maximum suppressor to determine the ratio of both waves. The pH* values of these solutions were measured, but with regard to difficulties in defining pH ($K_a \approx 10^{-15}$ for EG[22]) the values are only relative ones. The dependence of pH* on composition of the solutions

TABLE II
The Dependence of pH* of 0·1M-LiCl Solutions on the Composition of EG–H₂O Mixtures[a]

| % Vol. of EG | 0 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| With fuchsine | 6·6 | 6·4 | 5·5 | 5·1 | 5·0 | 5·1 | 5·1 | 5·4 | 5·8 | 5·8 | 6·8 |
| Without fuchsine | 6·1 | 5·8 | 5·8 | 5·8 | 5·9 | 5·8 | 5·8 | 6·0 | 6·2 | 6·5 | 6·5 |

[a]Solutions from which dissolved air was not removed. All measurements at 24·5°C. See the footnote on p. 668.

with and without fuchsine passes through a minimum which in the latter case is not so marked (see Table II). Both curves have the same trend as the dependence of $i_d \sqrt{\eta}$ on the composition (Fig. 2, curve 2). Considering the preceding reasons, we do not assume this curve to be a quantitative observation because the influence of pH was not eliminated. We only can conclude that the solubility of air oxygen in EG at 25°C is greater than in water and we estimate it to be about $10^{-3}$ mol/l. The ratio of the heights of both oxygen waves remains constant at $1 \cdot 0 \pm 0 \cdot 1$, which rather confirms the assumption that solvation of dissolved oxygen does not change in water–EG mixtures or in our 99·7 w.% EG.

Possibility of polarographic measurements in suspensions was already verified[23-25], however, for quantitative measurements specific conditions were required. In this work such conditions were not fulfilled because of requirements of a qualitative comparison only. It is worthy to point out that the removal of oxygen from suspension of $TH_2$ in EG is a very time-consuming procedure. It is possible that the crystals of $TH_2$ contain sorbed oxygen which slowly penetrates into the liquid. Difficulties with oxygen removal even from true solutions of aromatic compounds is a known phenomenon frequently encountered in the preparation of samples for NMR spectroscopy[26].

Also the shape of the polarographic capillary tip is important in the measurements under reduced pressure. The most convenient case would be the Smoleř horizontal capillary[27] or a capillary with a sloped tip to prevent "landing" of gas bubbles which go up to the solution level during evacuation of the cell.

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