

Photopotential and photocurrent induced by an aqueous solution of aliphatic alcohols

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Abstract

This paper deals with the photogalvanic behaviour of aliphatic alcohols in aqueous solution. It is found that UV-illumination causes the appearance of photopotential and photocurrent. The maximal values of the electrode potential and energy of the photogalvanic cell depend on the type of the alcohol used, its concentration, the temperature and the pH of the irradiated solution. An important characteristic of the phenomenon observed is its reversibility. After discharge of a photogalvanic cell by application of an external load in the circuit, a subsequent irradiation repeatedly leads to the appearance of photoinduced electrode potential and photocurrent. A possible mechanism of the photogalvanic effect is discussed.

Keywords: Aliphatic alcohols ; Photoelectrochemical properties; Photogalvanic effect of water-alcohol mixtures ; Transformation of energy of UV into electric energy

1. Introduction

There have been a number of extensive studies on the photoelectrochemical behaviour of several organic compounds since 1927. The most striking feature of all investigations in this field is that they are mainly directed to light-induced redox processes, including substances which absorb visible light, and especially synthetic and natural dyes, their derivatives and analogues (for example Refs. [1–9]).

The photogalvanic properties of alkylpyridinium salts in aqueous solutions have been discussed previously in Refs. [10–12]. In the course of these studies an appearance of photopotential was found when an aqueous solution of methanol was irradiated. It is the purpose of this paper to study this finding more comprehensively.

2. Experimental details

A schematic representation of the experimental set-up is given in Fig. 1. The cell consists of two chambers, light and dark, connected by an agar-agar bridge. Both chambers are the same size, 2.8 cm × 2.0 cm × 1.0 cm.

Platinum coil electrode (platinum wire, 0.5 mm in diameter and 200 mm in length) was sealed in a standard taper

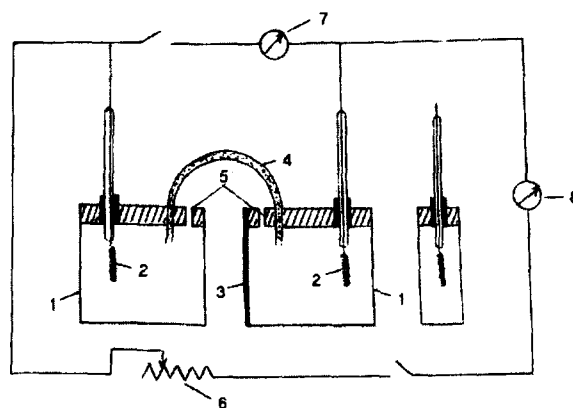


Fig. 1. Experimental set-up: 1, quartz plate; 2, platinum wire electrode; 3, membrane opaque to UV light; 4, agar agar bridge; 5, inlet for maintaining argon atmosphere above the solution; 6, external load (4000 Ω); 7, digital millivoltmeter; 8, microamperometer.

Pyrex joint, leaving 10 mm exposed in the irradiated part of the cell. The reference electrode has exactly the same dimensions as the indicator electrode. It was supported in the non-irradiated part of the cell. The electrodes were cleaned before use with a mixture of hydrochloric and nitric acid (1:3) for 10 s and then rinsed with distilled water. The cell was discharged by applying an external load.

Methanol and ethanol of reagent grade were refluxed for 24 h over calcium oxide and then fractionally distilled. A similar procedure was applied to the purification of

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compounds 3–5 except that sodium was used instead of calcium. Benzyl alcohol (6) and 1,2-dioxyethane (7) were obtained from Merck (spectroscopic grade). Water obtained by a distillation of ordinary distilled water over alkaline potassium permanganate in an all-glass still was used in all experiments. Solutions were purged with argon (99.999%) for 20 min before irradiation.

The samples (5 cm³) were placed in the thermostatically controlled irradiated and non-irradiated parts of the cell. The cell was exposed to UV polychromatic light under standard conditions.

UV irradiation was obtained from a medium pressure mercury arc lamp. The light quanta falling on the quartz cell were counted using an oxalate actinometer (1.27×10^{16} quanta cm⁻³ s⁻¹). The photopotential U was measured by a precise digital millivoltmeter (type OP-206/1, Radelkis) against the Pt-reference electrode, immersed in the non-irradiated solution of the corresponding alcohol. The electric photocurrent I arising in the circuit, including external load, was registered by a microammeter (type F.95, Russia).

3. Results and discussion

The irradiation of aqueous solutions of compounds 1–9 by polychromatic UV light results in the generation of a negative electrode potential, which increases gradually during the time of irradiation. Compounds 1–9 are of the form R-O-R': 1, R=CH₃, R'=H; 2, R=C₂H₅, R'=H; 3, R=n-C₃H₇, R'=H; 4, R=i-C₃H₇, R'=H; 5, R=t-C₄H₉, R'=H; 6, R=C₆H₅CH₂, R'=H; 7, R=OHCH₂CH₂, R'=H; 8, R=C₆H₅, R'=H; 9, R=CH₃, R'=CH₃.

The photopotential–time curves obtained are shown in Fig. 2. After the maximal value of electric photopotential was reached the cell was discharged. As can be seen from Fig. 3, the observed voltage–current dependences of the charged cells in all cases do not deviate from the rectangular shape. The energy Q was determined by a graphical integration of the dependence $UI=f(t)$, presented in Fig. 4.

In order to choose between the photovoltaic and photogalvanic route of generation of the photoinduced electric potential, a water–methanol solution was irradiated without an indicator electrode. The maximal value of the photopotential found was almost the same as those registered with the Pt-electrode immersed in the irradiated part of the cell. These data clearly show that the photoinduced electrode potential is due to a photogalvanic effect.

After the discharge of the cell, the subsequent irradiation of the same organic solute leads repeatedly to the generation of an electric potential (Fig. 5).

The data from Fig. 2 allow some conclusions concerning the relation between the structural peculiarities of the alcohols studied and their photogalvanic activity. The highest values of the photopotential U and energy Q of the cell were registered when solutions of low molecular weight alcohols (compounds 1–4) were illuminated. The introduction of a phenyl

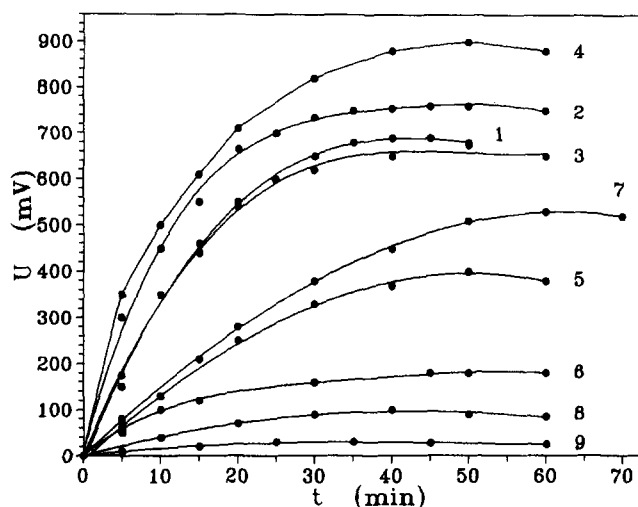


Fig. 2. Dependence of electrode photopotential U on the duration t of the UV irradiation of aqueous solutions of compounds 1–9.

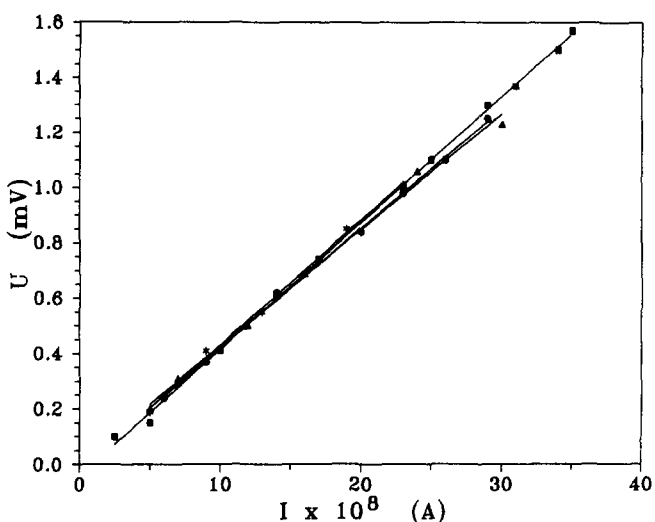


Fig. 3. Voltage–current characteristic of a charged cell containing 20 vol.% aqueous solutions of 1–4: ■, 1; ●, 2; *, 3; ▲, 4.

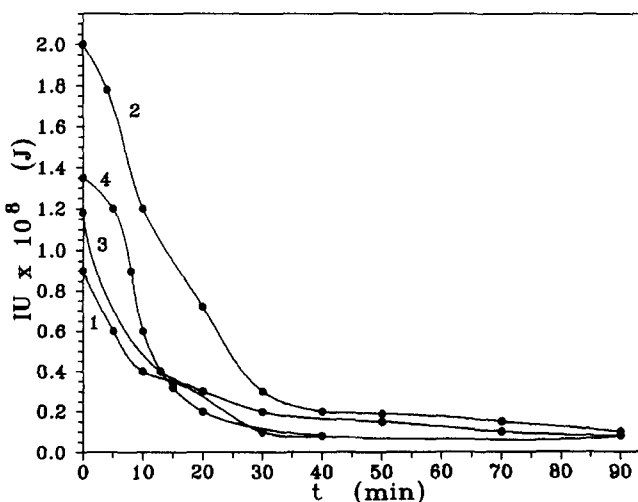


Fig. 4. Plots of the function $UI=f(t)$: U (V), electrode photopotential; I (A), electric photocurrent; t (min), time after the end of irradiation. External load $R=4000 \Omega$; 20 vol.% aqueous solutions of compounds 1–4.

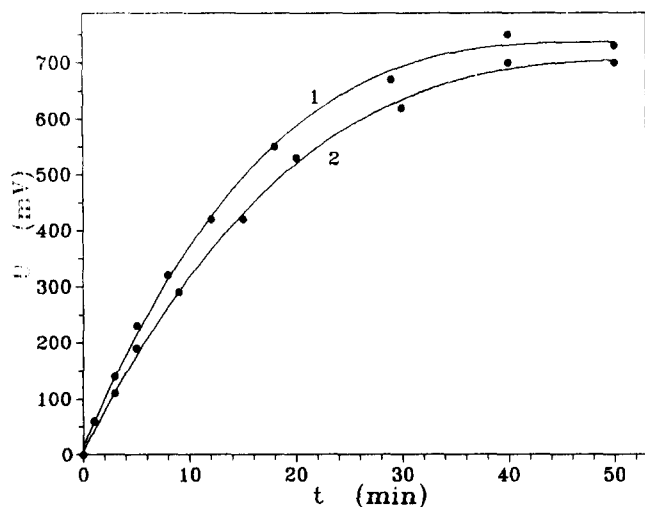


Fig. 5. Electrode photopotential U vs. the duration t of UV irradiation of compound 2 (20 vol.% aqueous solutions): curve 1, primary irradiation; curve 2, irradiation after discharge of the cell.

radical into the hydrocarbon chain (compound 6) decreases the U and Q values. An important structural feature consists in the fact that the change of an alkyl group to a phenyl group causes the disappearance of the photogalvanic properties of the organic solute (compound 8). An analogous effect is produced by the substitution of hydroxy hydrogen with an aliphatic residue (compound 9).

To assess the possible influence of the alcohol concentration on the effect observed, several experiments with compounds 1, 4 and 7 were carried out. The data found are presented in Fig. 6. The lowering of the concentration gradually leads to a decrease in the photogalvanic effect. At concentrations below 1×10^{-4} vol.% (molar fraction, about 10^{-7}) no potential was registered. On the contrary, an increase in the concentration above 20 vol.% (molar fraction, about 4×10^{-1}) diminishes the maximal values of the photopotential that arises. Somehow compound 7 deviates from the common dependence outlined. It was found that the opti-

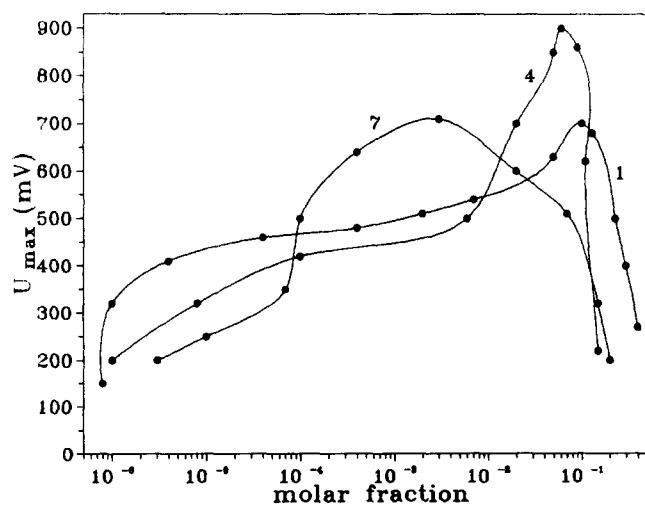


Fig. 6. Dependence of electrode photopotential (maximal values) on the molar fractions of compounds 1, 4, 7 in the irradiated solutions.

mal concentration in this case is considerably lower, about 1 vol.%.

A pH dependence of the photopotential was observed. Small variations in pH remain ineffective, but a significant change to lower (pH 3) or higher (pH 11) pH values of the irradiated solutions causes a rise in the photopotential and photocurrent. In particular, the water–ethyleneglycol system is especially sensitive to the pH of the irradiated solutions. Enhancement of the basicity leads to a substantial rise in the photogalvanic cell energy.

It was found that the temperature rise causes an increase in the photopotential. This tendency holds true for all water–alcohol solutions but it is typical for compound 7. The comparative experiments (with and without oxygen) unequivocally show that the presence of atmospheric oxygen in the irradiated solutions decreases the photopotential arise.

At least two alternative explanations of the phenomenon observed are conceivable. The first line of reasoning is to assume that the photogalvanic effect arises as a result of phototransformations of the irradiated alcohol, or one can assume that our findings are due to the specific nature of the alcohol–water mixture.

The absorption spectra of aliphatic alcohols consist of continuous bands, extending from 220 nm to the far UV region. The lowest excited electronic state of the methanol molecule is due to an $n \rightarrow \sigma^*$ transition. The high intensity absorption band which corresponds to this transition is at 185 nm. As the emission at 185 nm of the medium pressure mercury arc lamp is strongly absorbed by the impurities of fused quartz glass, it is evident that in our experimental conditions the photogalvanic properties of low molecular weight alcohols can eventually arise from their low intensity absorption in the region 200–220 nm.

In our recent study [13] of the photochemical behaviour of methanol and related compounds in aqueous solution, it has been established that low energy UV irradiation causes photo-oxidation of methanol to formic acid. Numerous studies in this field (for example Refs. [14–16]) have shown that the primary process is the formation of the corresponding aldehyde. Our results indicated that the presence of oxygen is an important factor in the effectiveness of the photoprocess involved. The intermediate formation of hydroperoxyhydroxymethane was proposed. It was proved that such a process does not proceed with *n*-PrOH, *i*-PrOH and *t*-BuOH.

The comparative examination of these data with the results in the present paper reveals that the photogalvanic properties of aliphatic alcohols do not ensue from the low energy UV absorption of these compounds. In this sense it is instructive to note the following peculiarities.

(i) Only the water–alcohol mixture possesses photogalvanic properties. The UV illumination of low molecular weight alcohols in the pure state does not lead to a photogalvanic effect. At the same time, as shown by Roussi and Beugelmans [17], the UV irradiation of pure methanol causes the formation of formic acid.

(ii) There is a clear dependence of the generated photopotential on the alcohol molar fraction.

(iii) Contrary to the case considered in Ref. [13], the presence of atmospheric oxygen decreases the magnitude of the effect involved.

(iv) A cyclic charging–discharging process of the photogalvanic cell (Fig. 5) without any use of additional reagents is realized. Comparatively, the photo-oxidation of methanol is a irreversible reaction. The photogalvanic properties of water–alcohol mixtures cannot be related to a reversible redox process.

Another explanation of the phenomenon found is to assume that it ensues from some specific characteristics of the aqueous solution of low molecular weight alcohols. Their properties are of substantial interest in many fields of enquiry. The alcohol–water mixtures exhibit abnormalities such as a viscosity–composition maximum or negative relative partial volumes in dilute aqueous solution. Such peculiarities can be generally attributed to the bifunctional nature of the solute molecules. The hydrophobic hydrocarbon group may be imagined as resisting the pull into solution exerted by the hydrophilic hydroxyl groups, which can form hydrogen bonds with the solvent molecules as either proton donor or proton acceptor.

The hydrogen bonding which plays a principal role in the interpretation of the components cannot alone account for the observed oddities in the water–alcohol mixtures. One can assume that they are structural in origin and will eventually be understood in the light of full knowledge of the structural peculiarities of the water–alcohol mixtures.

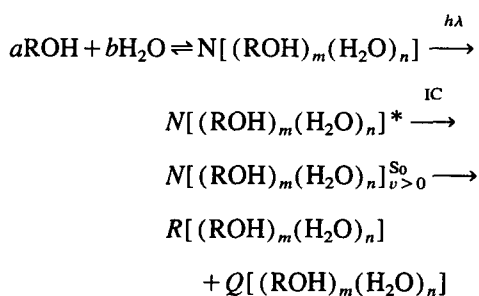
It is as yet difficult to rationalize the photogalvanic behaviour of the aqueous solutions of aliphatic alcohols. However, any mechanism proposed should be consistent with the thermodynamic excess functions of mixing of the lower monohydric alcohols with water. As mentioned above, the maximal photogalvanic effect of compounds 1–4 arises at alcohol concentrations in the molar fraction range 0.15–0.25. It is noteworthy that in the same concentration range the $T\Delta S$ term in the excess Gibbs free energy function for these compounds exhibits a well-defined minimum [18]. There are important parameters of the alcohol–water mixtures which are characterized by extreme values in the same concentration range. The partial molar volume for the ethanol–water system at 25 °C has a minimal value (maximal contraction) at an ethanol molar fraction of 0.2. Analogously the heats of mixing with water at 25 °C of MeOH, EtOH, *n*-PrOH and *t*-BuOH have a clear exothermic maximum in the molar fraction range 0.25–0.4. It may also be noted that the macroscopic viscosities of MeOH–H₂O and EtOH–H₂O systems are maximal at alcohol molar fractions of approximately 0.25 [18].

It is evident that the interpretation of the thermodynamic excess functions is not eased by virtual certainty because they are, at the simplest, the resultant of opposed contributions. Nevertheless, one can assume that these data as well as the concentration dependence of photopotential found have a common origin, related to the outlined large entropy loss.

Normally, this would denote the establishment of order by the satisfaction of attractive forces, leading to the enhancement of the absorption properties of the water alcohol mixtures to the UV light. In any event it is notable that the sound absorption in water–alcohol mixtures exhibits a clear maximum at alcohol molar fractions of 0.2–0.35 [19].

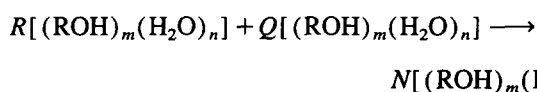
Following such a line of reasoning it may be inferred that the UV irradiation causes some important changes in the macromolecular structure of the water–alcohol aggregates. As mentioned elsewhere [20], the low intensity bands extending from 230 to 320 nm in the UV spectra of aqueous solutions of aliphatic alcohols may be attributed to the corresponding water–alcohol aggregates, which thermodynamic characteristics are close to those of two- or three-dimensional polymers [21].

It seems, from the results presented, that there is substantial indirect evidence for the following processes:



$$a + b = N(m + n)$$

On absorption of $\lambda = 220$ nm light the alcohol–water aggregate is promoted to an excited state. As a result of an internal conversion the high energy vibrational levels of the aggregate ground state $N[(\text{ROH})_m(\text{H}_2\text{O})_n]_{\nu>0}$ are populated. It collapses to new kinetically independent particles, possessing specific absorption ability on the Pt-electrode. This results in the transformation of the double electric layer and involves the appearance of electric potential. The reverse process.



gives rise to a gradual diminution of the photopotential. Additionally, one can conclude that the strong adsorption on the Pt electrode of molecules containing aromatic ring systems [22,23] is a possible reason for the vanishing of the photogalvanic effect.

A more comprehensive study on the photogalvanic properties of the water–alcohol mixtures is in progress.

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