EFFECT OF TEMPERATURE ON THE REDUCTION OF ORGANIC COMPOUNDS AT THE DROPPING MERCURY ELECTRODE

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In the practice of polarographic analysis it is known that the magnitude of the diffusion current largely depends on the operating temperature. The effect of the temperature on the diffusion current may be represented by Ilkovic's equation:

$$i_d = 605\, n\, D^{1/2}\, m^{2/3}\, t^{1/6} C, \qquad (1)$$

where i_d is the diffusion current in μA); n is the number of electrons participating in the reduction of one molecule; D is the diffusion coefficient of the molecules undergoing reduction (in $cm^2 \cdot sec^{-1}$); m is the weight of mercury flowing from the capillary per second (in mg); t is the period of formation (in seconds) of each drop of mercury; C is the concentration of reacting substance (in mmole/liter).

Starting from the above expression Kolthof and Lingane [1] obtained the following expression for the temperature coefficient of the diffusion current of the ions undergoing reduction (for temperatures around 25°C):

$$\frac{1}{i_d} \cdot \frac{di_d}{dT} = 0.0026 + \frac{1}{2\lambda_0} \cdot \frac{d\lambda_0}{dT}, \qquad (2)$$

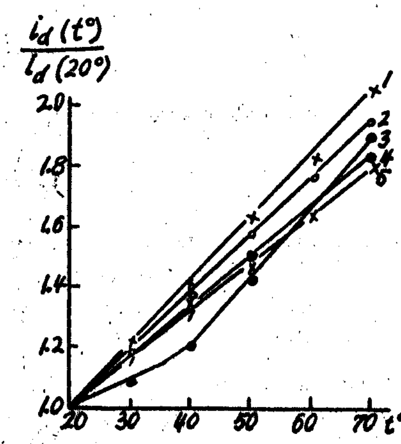
where λ_0 is the equivalent ionic conductivity at infinite dilution and for the absolute temperature T.

The first term on the right-hand side of the equation is much smaller than the second; consequently the temperature coefficient is mainly a function of the temperature coefficient of the equivalent conductivity of the ions being reduced. The temperature coefficients of the equivalent conductivity of the majority of ions lie within the range 0.02-0.027$^{\circ -1}$ with the exception of H^+ and OH^-, whose respective values are 0.0157 and 0.018$^{\circ -1}$. Hence the temperature coefficient of the diffusion current of the majority of ions must have a value within the range of 1.3-1.6% per degree and must be close to 1.05% per degree for dissociation of hydrogen ions.

The experimental values of the temperature coefficients of the diffusion current of ions of various metals for temperatures of 20 to 50° vary within the range of 1.3 to 2.3% per degree [1] and are in sufficiently good agreement with the theoretical values.

Diffusion currents of organic compounds as functions of the temperature have not been investigated.

In this paper we describe the results of a study of the effect of temperature on the polarographic reduction of benzaldehyde, butyraldehyde, chloracetamide, phenyl trichloroacetate, dibutylphthalate, maleic acid, and fumaric acid.



Influence of temperature on the reduction of organic compounds.
1) Benzaldehyde; 2) butyraldehyde; 3) phenyl trichloroacetate; 4) chloracetamide; 5) maleic and fumaric acids.

The investigations were performed on the M-7 visual polarograph of the Gorky Chemical Research Institute [2,3]. Prior to the plotting of the polarograms the electrolyzer containing the solution of the test substance was placed in a thermostat in which a constant temperature was maintained with the help of a toluene thermoregulator and a variable current relay. The rate of flow of the mercury from the capillary was uniform throughout the investigation at one drop per four seconds. The characteristic of the capillary utilized in the work was $m^{2/3} t^{1/6} = 0.78$

$mg^{2/3}$ $sec^{-1/2}$. All the values of diffusion current on the diagram and in the tables have been converted for a capillary with a characteristic of 1.0 $mg^{2/3}$ $sec^{-1/2}$. The current strength was measured with the help of a mirror galvanometer whose current sensitivity was $0.58 \cdot 10^{-9}$ A/mm/m. The anode was a saturated calomel cell whose potential was taken as zero. The applied voltage was measured with the help of a voltmeter accurate to 0.01 V.

The temperature dependence of the diffusion current of the investigated organic compounds is given in the diagram. The effect of temperature on the diffusion current and half-wave potential of butyraldehyde and maleic acid is shown by the experimental data presented in Tables 1 and 2.

TABLE 1

Effect of Temperature on the Reduction of Butyraldehyde in $(CH_3)_4NI$. C = 4.8 mmoles/liter

t° C	i_d μA	$\frac{i_d(t°)}{i_d(20°)}$	$-E_{1/2}$ B
20	15.3	1.00	1.88
30	18.0	1.18	1.88
40	25.5	1.67	1.88
50	29.6	1.93	1.90
60	30.0	1.96	1.88
70	30.6	2.00	1.86

TABLE 2

Effect of Temperature on the Reduction of Maleic Acid in $(CH_3)_4NI$. C = 4.0 mmoles/liter

t° C	i_d μA	$\frac{i_d(t°)}{i_d(20°)}$	$-E_{1/2}$ B
20	11.6	1.00	0.95
30	13.9	1.20	0.92
40	15.3	1.32	0.93
50	17.0	1.47	0.92
60	20.4	1.76	0.93
70	24.5	2.12	0.93

The diagram and the tables show that the temperature coefficient of all the investigated compounds with the exception of phenyl trichloroacetate remains constant with change of temperature from 20 to 70°, and that there is a straight-line dependence of the ratio of the diffusion current at a given temperature to the value at 20° on the temperature. The slope of the straight line varies for each compound investigated and varies slightly with the structure of the compound. In the case of benzaldehyde, for instance, the relation between $\frac{i_d(t°)}{i_d(20°)}$ and the temperature is represented by the formula:

$$\frac{i_d(t°)}{i_d(20°)} = 0.0021t \quad (3)$$

while for fumaric and maleic acids it is represented by:

$$\frac{i_d(t°)}{i_d(20°)} = 0.0156t. \quad (4)$$

The temperature coefficient of the diffusion current during reduction of organic compounds in the temperature range of 20 to 70° is 1.15-1.50% per degree. The experimental values show that the temperature coefficients of the diffusion current of organic compounds only differ slightly from the temperature coefficients of the diffusion current of the various ions and are close to the theoretical magnitude.

In the practice of polarography the temperature should be kept constant to within at least ±0.5° in order to ensure that the deviations of the diffusion current due to the temperature change should not exceed ±1.0%.

LITERATURE CITED

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