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Reports of the Academy of Sciences of the USSR

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1964

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Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1964. Volume 158, No. 6

PHYSICAL CHEMISTRY

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APPLICATION OF THE POLAROGRAPHIC METHOD FOR DETERMINING THE MOLECULAR WEIGHT OF POLYVINYL ALCOHOL

(Presented by Academician V. A. Kargin on 18 V 1964)

The use of polarographic maxima ([1]) for the study of high-molecular-weight substances may prove to be one of the successful methods for investigating certain properties of these compounds. It has been shown ([2–4,5]) that the size of the molecule plays the principal role in the suppression of polarographic maxima. On the basis of the suppression of the polarographic maximum of the first kind on the oxygen wave, we previously developed a method for determining the molecular weight of polystyrene, polyvinyltoluene, and polymethyl methacrylate ([6]). However, in adsorption polarographic analysis based on the suppression of maxima, maxima of both the first and second kinds are used to an equal extent ([7,8]).

The inconvenience of using maxima of the first kind consists in the fact that they appear within a rather narrow range of potentials and are not observed at all at the potentials of the zero charge of mercury. Most surface-active substances, however, are adsorbed most strongly in the region of the potential of zero charge of mercury.

In contrast to this, maxima of the second kind are most clearly expressed in the region of zero-charge potentials, and, at a sufficiently high electrolyte concentration, in the region of the potentials of the entire wave. Surface-active substances can suppress a maximum of the second kind at low concentration and over a broad range of potentials.

Our investigations consisted in determining the degree of lowering of the polarographic maximum of the second kind on the copper wave as a function of the magnitude of the molecular weight of polyvinyl alcohol.

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Fig. 1. Change in the height of a polarographic maximum of the second kind on the copper wave under the influence of one of the fractions of polyvinyl alcohol

Figure 1: Fig. 1. Change in the height of a polarographic maximum of the second kind on the copper wave under the influence of one of the fractions of polyvinyl alcohol

Experimental Part

The molecular weight of the polyvinyl alcohol fractions was determined viscometrically in distilled water at 20°. The molecular weight M and the degree of polymerization n were calculated from the formulas $M = \left(\frac{[\eta]^{1/\alpha}}{k}\right)$; $n = M/M_1$, where M_1 is the molecular weight of the structural unit of polyvinyl alcohol, equal to 44, $k = 8.87 \cdot 10^{-4}$, $\alpha = 0.62$.

Measurements were carried out on an LP-55A polarograph with a dropping mercury cathode. The period of complex formation in the electrolyte was 1.5 sec, the mass of a mercury drop $m = 4.76$ g/sec; the height of the mercury column $H = 65$ cm. Measurements were carried out in an electrolyzer with an internal anode. Four ml of background solution (1 N solution of KCl in water), in which the depolarizer was dissolved ($3 \cdot 10^{-3}$ M $CuSO_4$), were poured into the electrolyzer. The solution was thoroughly purged with nitrogen and the maximum of the second kind was recorded. Then 0.4 ml of a standard solution of the polyvinyl alcohol fraction, concentration $2.5 \cdot 10^{-2}$%, was added to the solution, purged with nitrogen, and the wave was again recorded. The concentration of polyvinyl alcohol in the electrolyzer was $2.5 \cdot 10^{-3}$%. As a result of adsorption of polyvinyl alcohol molecules, a change in the height and shape of the wave occurs –suppress-

tion of a maximum of the second kind over a wide range of potentials–from −0.6 to −1.7 V (Fig. 1).

Measurements of the wave height h of the maximum of the second kind were carried out at one potential; the change in the height of the maximum Δh was expressed as a percentage of the initial height of the standard maximum.

To eliminate the possibility of contamination by surface-active substances from the equipment, vessels with rubber and cork stoppers, filter paper, etc., were excluded. The capillary was fixed in the cell by means of a ground joint; concentrated sulfuric acid, distilled water, and bidistilled water were used for washing the cell and volumetric glassware. Working solutions were prepared with bidistilled water. The salt required for preparing the supporting electrolyte was recrystallized and calcined to remove surface-active substances.

Fig. 1. Change in the height of a polarographic maximum of the second kind on the copper wave under the influence of one of the fractions of polyvinyl alcohol

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Fig. 2. Dependence of the decrease in the maximum of the second kind on the copper wave on the molecular weight of the polyvinyl alcohol fraction

Figure 2: Fig. 2. Dependence of the decrease in the maximum of the second kind on the copper wave on the molecular weight of the polyvinyl alcohol fraction

Results of the investigations

The influence on the polarographic maximum of the second kind on the copper wave was studied for eight fractions of polyvinyl alcohol with different molecular weights.

Fig. 2. Dependence of the decrease in the maximum of the second kind on the copper wave on the molecular weight of the polyvinyl alcohol fraction

As can be seen from the graph of the dependence of the degree of decrease in the maximum height on the molecular weight of the polyvinyl alcohol fractions (Fig. 2), the degree of decrease in the maximum, and consequently also the magnitude of adsorption of the polymer molecules, increases as the molecular weight of the fractions decreases. This graph can be used as a calibration graph in determining the molecular weight of unknown fractions of polyvinyl alcohol. We studied the influence on the maximum of the second kind of a mixture of two fractions of polyvinyl alcohol, taken in equal amounts, with a total concentration of $2.5 \cdot 10^{-2}$%. Studying fractions with molecular weights $110 \cdot 10^3$ and $50 \cdot 10^3$, we obtained points corresponding to the mean value of these quantities, i.e., $80 \cdot 10^3$ (points in the form of triangles in Fig. 2); taking fractions with molecular weights $59 \cdot 10^3$ and $50 \cdot 10^3$, we obtained points corresponding to a molecular weight of $55 \cdot 10^3$.

The results of this experiment make it possible to determine, by this method, both fractionated and unfractionated samples of polyvinyl alcohol. Table 1 gives data from the statistical treatment [9] of the results of determining the molecular weight of polyvinyl alcohol, from which it is seen that the relative error in the determinations of molecular weight by this method does not exceed ±4.0%.

Table 1

Results of statistical processing of data on determining the molecular weight of polyvinyl alcohol by the polarographic method

Specimen Nos.	M	n	$\overline{\Delta h}$, %	a	t_a	S^3	$S_{\overline{x}}$	ε_{rel}	$\overline{\Delta h}$, % $\pm t_a S_{\overline{x}}$
1	$100 \cdot 10^3$	6	37.7	0.95	2.571	3.77	0.412	0.8	37.7± 0.3
2	$80 \cdot 10^3$	6	41.5	0.95	2.571	2.24	0.610	3.8	41.5± 1.6

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Specimen Nos.	M	n	$\overline{\Delta h}$, %	a	t_a	S^3	$S_{\overline{x}}$	ε_{rel}	$\overline{\Delta h}$, % $\pm t_a S_{\overline{x}}$
3	$50 \cdot 10^3$	6	51.3	0.95	2.571	1.41	0.485	2.4	51.3 ± 1.2

For comparison, we attempted to use the first-kind maximum in determining the molecular weight of polyvinyl alcohol. Changes in the height of the first-kind maximum on the copper wave ($3 \cdot 10^{-3}$ M $CuSO_4$) in a 0.01 N KCl solution in water were as follows:

Mol. wt. $\cdot 10^{-3}$	110	100	80	71	68	50	3
Δh, %	30.2	30.2	30.2	30	30.5	30.2	48

From these data it is evident that the value of Δh for the first-kind maximum on the copper wave changes hardly at all with decreasing molecular weight. This is explained by the fact that the first-kind maximum on the copper wave appears at potentials of -0.4, -0.5 V, whereas adsorption of polyvinyl alcohol occurs most completely at more negative potentials, which is clearly seen in the suppression of the second-kind maximum of copper, expressed in the potential region of the entire wave.

Consequently, in determining the molecular weight of polyvinyl alcohol by the polarographic method, it is more effective to use second-kind maxima.

The proper combination of first- and second-kind maxima in the study of polymers makes it possible to find the most sensitive adsorption region for each polymer. The polarographic method for determining the molecular weight of polyvinyl alcohol is sufficiently simple, does not require large expenditures of time, and, when a calibration graph is available, can be successfully applied in carrying out serial analyses.

The authors express their heartfelt gratitude to L. N. Veselovskaya for providing individual fractions of polyvinyl alcohol for the investigation.

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Received
15 V 1964

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Note: Figure translations are in progress. See original paper for figures.

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