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**Abstract**

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# PURIFICATION OF METHYL METHACRYLATE BY THE ZONE-MELTING METHOD

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Experience in the polymer industry shows that the production of very pure monomers can be achieved by a single rectification; however, this requires overcoming great technical difficulties and expense—rectifying columns up to 100 m high are needed. A somewhat different way of solving this problem appears possible, namely, by combining methods of rectification and multiple recrystallization by the zone-melting method. Zone melting (z. m.) has proved highly effective in the purification of metals. In this way metals can be obtained with an impurity content of no more than $10^{-6} \div 10^{-7}\%$. Such results are not achieved by any of the other known purification methods. At present, industrial methods of continuous z. m. are known, which is important for flow methods of production [1]. It is natural to attempt to apply the z. m. method to the purification of monomers. During purification the monomer must be in the solid state. The crystallization temperatures of most organic monomers lie in the range from +15 to −165°. The refrigerants required for this—ordinary ice, solid carbon dioxide, and liquid nitrogen—are obtained in large quantities and are available for industrial use. Thus, the basic necessary conditions exist for using zone melting in purification in industry. Only a few exploratory studies are known on the application of z. m. to the purification of high-melting organic substances (benzene [2], naphthalene [1], benzoic acid [3], anthracene [4]). All this has led to the need for scientific development of the zone-melting method for monomers.

The present work is the result of initial experiments. The following basic regularities of the z. m. method were used in the work. The principal index of the effectiveness of z. m. is the distribution coefficient $k$, which is determined by the ratio of impurity concentrations in the liquid and solid phases during z. m., $k = \frac{C_{\text{tv}}}{C_{\text{zh}}}$. Experimentally it can be determined from experiments on directional crystallization using the equation

$$\frac{C}{C_0} = k(1-g)^{k-1}, \tag{1}$$

where $g$ is the fraction of the solidified part, $C$ is the impurity concentration for the point $g$, and $C_0$ is the initial impurity concentration.

Such a distribution of impurities in the solid is achieved by gradual freezing of the liquid with an initial impurity concentration $C_0$, provided that equilibrium in the liquid phase always has time to be reestablished (intensive stirring), and diffusion in the solid phase can be neglected. Maximum separation (purification) is achieved when the distribution coefficient $k$ becomes equal to $k_0$, determined by the thermodynamic conditions of equilibrium.

An approximate calculation of $k_0$ can be made by formula (5)

$$N_2 = \frac{\Delta H \cdot \Delta T}{RT^2(1-k_0)}, \tag{2}$$

where $\Delta H$ is the heat of fusion, $N_2$ is the mole fraction of the impurity, $\Delta T$ is the depression of the melting temperature, and $T$ is the melting temperature.

$k$ and $k_0$ are related by

$$k = \frac{k_0}{k_0 + (1-k_0)e^{-f\delta/D}}, \tag{3}$$

where $f$ is the crystal growth rate, cm/sec, $D$ is the diffusion coefficient, $\mathrm{cm}^2$/sec, and $\delta$ is the thickness of the diffusion layer of liquid at the boundary with the solid phase.

For zone melting, the equation of the impurity distribution curve after $n$ passes ([6,7]) in differential form is

$$\frac{l}{k}\, dC_n(x) = [C_{n-1}(x+l) - C_n(x)]\, dx, \tag{4}$$

where $C_n(x)$ is the impurity concentration at point $x$ after $n$ zone passes, and $l$ is the length of the sample. The solution of this equation gives the relation between the distribution coefficient and the degree of purification of the substance from the impurity for any number of passes.

The last question is the determination of the limiting degree of purification as $n \to \infty$, which is defined by the equation:

$$C(x) = Ae^{Bx}. \tag{5}$$

$A$ and $B$ are constants determined by the equalities

$$k = \frac{Bl}{e^{Bl}-1}, \qquad A = \frac{C_0 BL}{e^{BL}-1},$$

where $l$ is the zone length; all other notation is as before.

## Experimental Part

MMA was selected as the object of study. Its crystallization temperature is $\sim -50^{\circ}$; therefore liquid nitrogen served as the coolant. MMA was poured to half the level into a tin tray 10 cm long, 2 cm wide, and 3.5 cm high. The nitrogen level was approximately half a centimeter higher than the level of the substance. A flat spiral for melting MMA was made from constantan wire 0.5-0.7 mm in diameter, which was fastened in a T-shaped plastic plate, the arms of which slid along guiding plastic rods clamped in four stands. The spiral was heated by alternating current from the mains, $I = 6$–$9$ A. By moving the spiral immersed in the solid MMA, zone melting was carried out. The width of the melting zone was $l = 10$ mm. Passage of the entire tray by the spiral was accomplished in 10-20 min, which corresponds to 0.017-0.008 cm/sec.

The value of $k$ was obtained from an experiment on directional crystallization and proved to be 0.35 according to equation (1). Because the true values of $\delta$ and $D$ for MMA were unknown to us, for calculation of $k_0$ by equation (3) we had to use the value $\delta/D = 100$ sec/cm ([1]). $k_0 \approx 0.16$. The initial MMA had a purity of 99.2%. After five passes, the impurity content changed from 0.8 to 0.1%, which gave a purity of 99.9% and $C/C_0 = 0.12$. From the graphs given in work ([1]) (the graphs were obtained by solving the original differential equation (4)), for the specified parameter values one can obtain for $C/C_0$ the value 0.09, close to the experi-

experimental. For MMA, the limiting degree of purification, found from equation (6), is obtained as equal to $C/C_0 = 10^{-7}$. The purity was determined by the cryoscopic method [8].

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