THE HYDROCARBON CONCENTRATION DISTRIBUTION IN THE HOMOLOGOUS SERIES FOR INDUSTRIAL AND NATURAL MIXTURES

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The data of many investigators [1-5] show that there is a fixed dependence between the concentration of members of a homologous series and the number of carbon atoms in them for different complex industrial and natural mixtures. Typical hydrocarbon concentration distribution curves within the homologous series are given in Fig. 1 (the original data were taken from [1]).

Finding a quantitative expression for the hydrocarbon concentration distribution within the homologous series (Cn) would make it possible to solve some of the problems which are important in the analytical chemistry of industrial mixtures. Knowing such a dependence would make it possible to calculate the concentration of the components in high-boiling fractions from data on the composition of the low-boiling fractions and, in this way, to avoid partially the difficulties associated with the analysis of high-boiling, complex mixtures.

A detailed analysis of the low-boiling and medium-boiling fractions of industrial mixtures shows the presence of tens or hundreds of components, even in the narrow fractions of these mixtures, in which case the number of components increases approximately in a geometric progression as the boiling temperature of the mixture increases; at the same time, the difficulty in figuring out the quantitative and qualitative composition of these mixtures increases even more rapidly. All of this creates the necessity of finding the most general relationships in the concentrations of the components of complex mixtures which might make a basis for calculating the concentration of the high-boiling components from the concentration of their low-boiling homologs. In addition, a knowledge of the quantitative dependence for Cn might be used to evaluate the reliability of the results of an analysis of compounds of a given series.

In order to clarify the nature of the change in the composition of industrial mixtures of petroleum products obtained during various technological processes, it is more expedient to compare the values of several coefficients for the equation which relates the concentration and the number of carbon atoms for the members of the homologous series than to compare direct data on the concentrations of tens of homologs.

The form of the distribution curve is reminiscent of a Gaussian curve, but it differs from it by the asymmetric position of its branches. It was established that the distribution curve for the homolog concentrations can be described by means of the equation:

\[
\ln \frac{C_i}{M_i} = \frac{n_i^2 + \beta}{an_i} + f,
\]

where \(C_i\) is the weight concentration of the i-th member of the homologous series, \(M_i\) is the molecular weight of the i-th member of the homologous series, \(n_i\) is the number of carbon atoms in the molecule of the i-th member of the homologous series, and \(\alpha, \beta, \text{ and } f\) are the coefficients which determine the form of the distribution curve and which are constant for a given complex mixture.

The parameter \(\beta\) determines the position of the maximum for the distribution curve along the \(n_i - n = \sqrt{\beta}\) axis. The values of the parameters and \(f\) are related with the maximum value of \(C_i/M_i\):

\[
\left( \ln \frac{C_i}{M_i} \right)_{\text{max}} = \frac{2\sqrt{\beta}}{\alpha} + f.
\]


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Fig. 1. Dependence of the concentration of the n-paraffins on the number of carbon atoms in petroleums: 1) Darius; 2) Ponka Siti; 3) Nort Smaier.

Fig. 2. Rectification of the concentration distribution curves for n-paraffins in the coordinates $\ln(C_i/M_i) - (n_i^2 + \beta)/n_i$ for the following petroleums: 1) Darius; 2) Ponka Siti; 3) Nort Smaier.

The rectified curves for the concentration distribution are shown in Fig. 2 in the coordinates

$$\ln \frac{C_i}{M_i} = \frac{n_i^2 + \beta}{n_i}.$$

The coefficient $\beta$ was found from the position of the maximum on the distribution curve. The tangent to the angle of slope for the straight line in these coordinates gives the values for the coefficient $\alpha$; the segment cut by the straight line on the $\ln C_i/M_i$ axis is equal to $f$. In those cases for which the maximum on the distribution curve is not within the limits of the narrow fraction which was analyzed, it is necessary to test several values of $\beta$ equal to the squares of consecutive whole numbers and to select the values of $\beta$ for which the deviation of the points from a straight line is a minimum.

In order to evaluate the possibility of using the equation given above for extrapolation calculations of the concentration, the composition distribution curves in the homologous series of some of the hydrocarbons which are present in a number of industrial and natural mixtures was rectified and the mean relative deviations were found for the concentrations, calculated by means of the indicated equation from measured values.

For the distribution curves of the normal paraffins in petroleums the mean relative deviation is 7-10% (data were used on the composition of petroleums from the Darius, Ponka Siti, and Nort Smaier [1], Romashkino [3] deposits and three other domestic petroleums which were analyzed at VNII NP). In the directly distilled naphtha fractions which boil up to 150 °C for three of the petroleums analyzed at the VNII NP, the concentration distribution was studied for the normal paraffins, the 2-methylalkanes, and 3-methylalkanes. In the naphthas from catalytic cracking (six samples) the concentration distribution was studied for the normal paraffins, 2-methylalkanes, and 1-alkanes. The relative deviation in these cases was about 10%. The absolute deviation is equal to 0.05-0.5% and is comparable in order of magnitude with the error of measuring the concentration.

The equation given above is also applicable to describing the concentration distribution for compounds as a function of the number of carbon atoms within different classes of compounds. The curves for the concentration distribution of aromatic olefins and cyclic olefinic hydrocarbons in naphthas from catalytic cracking are shown in Figs. 3 and 4 (the original data were taken from [5]). In Figs. 3 and 4 the ordinate for any point is equal to the total concentration of the isomeric compounds of the same type with a given number of carbon atoms.