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A METHOD FOR CALCULATING THE TEMPERATURE DEPENDENCE OF THE VISCOSITY OF LOW-MOLECULAR-WEIGHT ORGANIC LIQUIDS

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A simple algorithm is proposed for calculating the temperature dependence of the viscosity of low-molecular-weight organic liquids if at least one value of the viscosity of the liquids is known at a particular temperature.

Molecule association due to forces of various kinds (for example, H-bonds) results in more complex particles, whose molecular mass is naturally larger than that of the monomeric molecule.

The process of formation and break-down of the associates in a real organic liquid is an equilibrium one. Both monomeric and more complicated molecular complexes exist simultaneously in this liquid. Therefore, the molecular mass of particles in a real liquid should be considered as an average value of the mass of an i-meric particle mixture:

$$M_{tr} = \Sigma x_i M_i . \tag{1}$$

However, determination of the concentration x_i is difficult and, therefore, relation (1) cannot be used in practice. One can determine M_{tr} of these liquids conveniently and accurately from the dependence of viscosity or other properties of the liquid on the molecular mass of constituent particles, using accurate and reliable measurements of these properties.

Analysis of experimental viscosities of organic liquids with the molecular mass known exactly gave the dependence of the dynamic viscosity on the molecular mass [1]:

$$\eta = A \exp (kM) , \ \text{mPa} \cdot \text{sec} \tag{2}$$

which is valid for $M \leq 145$ kg/kmole. Here $A = 0.053737$; $k = a_0 + (a_1/T)$; $a_0 = -0.0172$; $a_1 = 10.97544$.

Relation (2) can be used to determine the true molecular mass M_{tr} of a real liquid from the viscosity $\eta(T_0)$ of the real liquid at a temperature T_0 in the range $T_{solid} < T_0 < T_{boill}$, if the liquid tends to form molecular complexes:

$$M_{tr} = \frac{\ln \eta (T_0) - \ln A (T_0)}{k (T_0)} . \tag{3}$$

Comparison of the molecular mass calculated from (3) with the molecular mass M, corresponding to the chemical empirical formula, determines the association degree of the liquid considered [2]:

$$\psi = M_{tr}/M .$$

Calculation of the degree of association ψ at various temperatures for a number of liquids [1] showed that ψ was independent of temperature in the range from T_{solid} to T_{boil}. Otherwise, the true molecular mass of the liquids is not a temperature function:

$$M_{tr} = \psi M . \tag{4}$$

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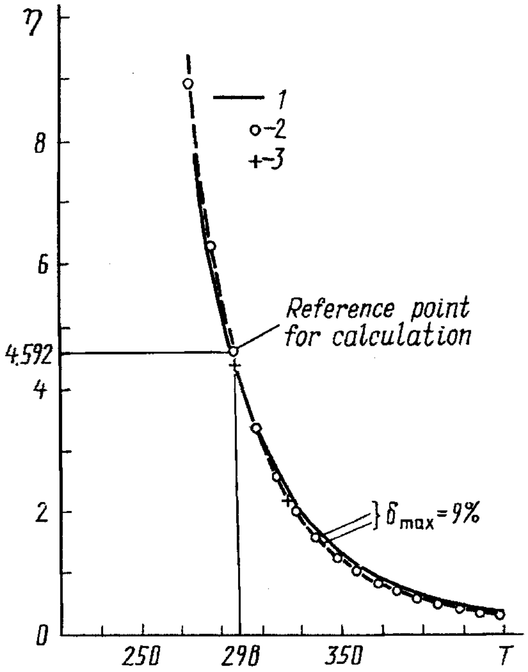

Fig. 1. Temperature dependence of viscosity of *n*-hexyl alcohol: 1) our prediction with $\eta = 4.592$ mPa·sec at $T = 298.15$ K [3]; 2) measurements of [3]; measurements of [4]. η, mPa·sec; T, K.

TABLE 1. Values of $k(T)$ and Predicted Viscosity for *n*-Hexyl Alcohol at Various Temperatures

T, K	$k(T)$, kmole/kg	$\eta(T)$, mPa·sec	T, K	$k(T)$, kmole/kg	$\eta(T)$, mPa·sec
230.15	0.0304882	54.1138	330.15	0.0160437	2.0443
240.15	0.0285024	34.4914	340.15	0.0150664	1.6379
250.15	0.0266754	22.7905	350.15	0.0141449	1.3290
260.15	0.0249888	15.5463	360.15	0.0132746	1.0909
270.15	0.0234497	10.9655	370.15	0.0124513	0.9051
280.15	0.0219770	7.8517	380.15	0.0116713	0.7584
290.15	0.0206267	5.7804	390.15	0.0109313	0.6412
298.15	0.0196118	4.5920	400.15	0.0102283	0.5467
300.15	0.0193665	4.3435	410.15	0.0095595	0.4697
310.15	0.0181875	3.3243	420.15	0.0089226	0.4066
320.15	0.0170821	2.5872			

It follows then that considering complex formation, it is possible to obtain the temperature function of the viscosity with a single viscosity value at a certain temperature:

$$\ln \eta\,(T) = \ln A\,(T) + k\,(T)\,M_{tr}\,. \tag{5}$$

The calculation method can be illustrated by predicting the temperature dependence of the viscosity for liquid *n*-hexyl alcohol (*n*-hexanol): $M = 102.17$ kg/kmole, η (298.15) = 4.592 mPa·sec [3].

In view of the above, a simple calculation algorithm can be presented as follows:

1) k (298.15) is evaluated (see Table 1):

$$k\,(298.15) = a_0 + a_1/T = -\,0.0172 + 10.97544/298.15 = 0.0196118\,;$$

2) in the region $M \leq 145$, in $A(T_0)$ is constant and equal to -2.923653;

3) the true molecular mass of *n*-hexanol is determined as

$$M_{tr} = \frac{\ln \eta\,(298) - \ln A\,(298)}{k\,(298.15)} = \frac{\ln 4.592 + 2.923653}{0.0196118} = 226.8 \text{ kg/kmole}\,;$$

4) $\eta(T)$ is calculated from equation (5) for $T = 230.15\text{-}420.15$ K with a step of 10°. The results are summarized in Table 1.

A comparison of the predicted and experimental viscosities of *n*-hexanol is given in Fig. 1, which confirms the reliability of the method proposed for calculating viscosities in the temperature range from T_{solid} to T_{boil}.

CONCLUSIONS

The method proposed here to calculate the temperature dependence of viscosity of organic liquids with molecular mass not exceeding 145 kg/kmole allows the entire temperature function $\eta = \eta(T)$ to be determined in the range of T_{solid} to T_{boil}, using a single known viscosity value η_0 at a certain temperature T_0.

NOTATION

η, dynamic viscosity; T, temperature; M_{tr}, molecular mass of an associate (complex); M, molecular mass; x_i, concentration of monomers, dimers, trimers, and other particles in the liquid; A, k, constants in equation (2); a_0, a_1, coefficients for evaluation of k; $\eta(T_0)$, dynamic viscosity at T_0; T_{solid}, solidification temperature of the liquid; T_{boil}, boiling temperature of the liquid; $A(T_0)$ and $k(T_0)$, values of the coefficients A and k at T_0; ψ, degree (number) of liquid association.

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