Viscosities of \( n \)-Alkylamines from 15 to 80\(^{\circ}\)C

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The viscosities of seven \( n \)-alkylamines from \( n \)-butylamine to \( n \)-decylamine were determined from 15 to 80\(^{\circ}\)C at 5\(^{\circ}\)C intervals. The intrinsic volumes were determined by extrapolation of the plot of fluidity against molar volume to zero fluidity and found to be a linear function of the number of carbon atoms. Plots of the logarithm of viscosity vs. reciprocal absolute temperature were almost linear. The energies of activation for viscous flow for the \( n \)-alkylamines were calculated and found to increase with increase in the carbon number. The \( B \) values, based on Hildebrand's equation and representing a measure of a molecule's resistance to transport of momentum, were calculated for each of the \( n \)-alkylamines. A modified form of the equation describing the change fluidity with temperature was then formulated. It is suggested that the activation energy for viscous flow consists of the sum of the energy required for the expansion of the void volume and the energy required to overcome intermolecular interactions. These energies were calculated and discussed.

KEY WORDS: \( n \)-alkylamines; viscosity; molar volume.

1. INTRODUCTION

Viscosities of liquids have been studied extensively since the last century. Numerous empirical and theoretical equations have been formulated to relate the variation with temperature, pressure and the bulk and structural properties of the liquids.\(^1\) However, the property is still not completely understood and continues to be studied. Most notable among the empirical equations used is the Andrade equation which relates the viscosity, \( \eta \), with the absolute temperature, \( T \), by an Arrhenius type of exponential function\(^2\) as in the following equation

\[
\eta = A e^{E/RT} \tag{1}
\]

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where $E$ is the activation energy for viscous flow, $R$ the gas constant and $A$ another constant.

Early in the century, Batschinski observed that the reciprocal of the viscosity, the fluidity, of non-associated liquids are linearly related to their molar volumes.\(^{(3)}\) Later, Hildebrand in a series of papers\(^{(4-6)}\) modified the original Batschinski equation to obtain

\[
\phi = B \frac{(V-V_o)}{V_o}
\]

where $\phi$ is the fluidity, $V$ the molar volume, $V_o$ the intrinsic volume defined as the molar volume at zero fluidity corresponding to the solid state volume but retaining rotational motion and $B$ is a constant which is a measure of the molecules' ability to absorb externally applied momentum due to its mass, shape and flexibility. The equation is only applicable to non-associated liquids.

We have previously determined the viscosities and molar volumes of series of long chain fatty acids,\(^{(7)}\) esters,\(^{(8)}\) and alcohols,\(^{(9)}\) with different carbon chainlengths at different temperatures and found that the Hildebrand and the Andrade equations can be combined into a more comprehensive equation to relate changes of viscosities of associated liquids with temperature and chain length.\(^{(9,10)}\)

Fatty alkylamines are important industrial chemicals used in the manufacture of cationic surfactants. The viscosities of the $n$-alkylamines longer than butylamine are difficult to obtain in the literature. It is thus the purpose of this study to furnish these data as well as to further test the validity of our combined equation reported earlier.

2. EXPERIMENTAL

Analytical reagent-grade $n$-alkylamines from $C_4$ to $C_{10}$ (Fluka, Chemie AG, Switzerland) with 99 percent purity and better were dried over molecular sieves before use. $n$-Butylamine was dried over potassium hydroxide pellets and fractionally distilled. The viscosity was measured using a Ubbelohde viscometer which was placed in a thermostatted water bath kept at $\pm 0.02^\circ C$. The viscometer was calibrated with double distilled water and triply distilled ethanol. The flow time for pure water at $25^\circ C$ was about 500 s. When measuring a viscosity, a series of flow times were recorded until at least three successive measurements agreed to $\pm 1.0$ of the average value.

The molar volumes were calculated from the densities determined using a pycnometer as described previously.\(^{(9)}\)