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Effect of Pressure on Viscosity of Higher Hydrocarbons and Their Mixtures

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Using the rolling-ball method the viscosity of seven pure hydrocarbons, having 25 or 26 carbon atoms, and three binary mixtures of them has been measured to 3450 bars at 37.8°, 60.0°, 98.8°, and 135°C. The compounds included isoparaffinic, cycloparaffinic, and aromatic types. The increase in viscosity with pressure was found to be strongly dependent on molecular structure. The viscosity-temperature coefficient $1/\eta(\partial\eta/\partial T)_p$ increased with increased pressure while the viscosity-pressure coefficient $1/\eta(\partial\eta/\partial P)_T$ decreased with increased temperature. The behavior of the binary mixtures corresponded within 5% over a range of 50–100 fold change in viscosity to that of the pure compounds equivalent to them in molecular weight and average molecular structure. This remarkable agreement is interpreted to mean that the viscosity of these compounds is some additive function of their constituent groups whether these groups are combined in the same or different molecules as long as the basic molecular symmetry is unchanged. The values of the Eyring theory $\Delta F_\pm$, $\Delta H_\pm{}^i$, $\Delta S_\pm$, and $\Delta V_\pm$ for these data are discussed. For the saturated compounds at constant temperature, an approximately linear relation was found between $\log \eta$ and $[(v/v_0)^4 - (v/v_0)^2]$ where v is the specific volume and η the absolute viscosity.

I. INTRODUCTION

THE viscosity of liquid substances has been studied intensively for many years because of the importance of the data both to engineering applications and to the fundamental problem of the liquid state. While the analyses of Frisch, Eyring, and Kincaid[1,2] have led to progress in understanding the problem of viscous motion, Bridgman has pointed out that the theory still needs some essential modification in the physical ideas.[3] The most extensive studies of viscosity as a function of pressure both as regards pressure range and materials studied are those of Bridgman.[3,4] Starting with Eyring's equation, Muhkerjee[5] has derived a relation between viscosity and specific volume which agrees well with Bridgman's data on the halogenated benzenes. However, the final form of Muhkerjee's expression does not afford a direct test of the ideas used in its derivation because the essential expressions are not in the final working equation. It seems worthwhile then to secure further data on the viscosity of pure substances as a function of temperature and pressure and to study them for their relationship to other specific properties of the material.

A research group at The Pennsylvania State University has synthesized over 230 high purity hydrocarbons containing from 8 to 50 carbon atoms per molecule, and including a wide variety of structure types.[6] Most of the hydrocarbons are in the C_{25} to C_{30} region. Numerous physical properties have been determined for each compound for the purpose of relating these properties to the molecular structure.[6] Thus there exists in this supply of hydrocarbons related groups of intensively studied high purity liquids which afford a unique opportunity for investigating the effect of structural variables on viscosity. The study of these liquids under pressure offers the further advantage of varying the specific volume at constant temperature, thus permitting separation of the two physical variables in their effect on viscosity.

The object of the work reported in this paper has been to determine the effect of pressure on the viscosity of a structurally related group of pure high molecular weight hydrocarbons and some binary mixtures of them. The present paper reports the experimental data obtained and certain interesting conclusions which were derived from them.

II. APPARATUS AND EXPERIMENTAL PROCEDURE

A rolling-ball viscometer of the type originated by Flowers[7] and first applied by Hersey and Shore to pressure viscometry[8] was used. The apparatus employs the empirical principle that the velocity with which a sphere moves down an inclined tube filled with liquid is a function of the liquid viscosity.

A 10-ml sample was enclosed in a 1/4-in. bore steel tube and the time interval required for a 3/16-in. steel ball to roll from one end to the other was measured to the nearest 1/100 sec by means of an electric clock. Pressure was transmitted to the confined pure liquid through a flexible brass bellows filled with the sample and connected to the roll-tube. The pressure was measured by the resistance change of a coil of manganin wire immersed in the hydraulic fluid and kept at room temperature. The resistance of manganin

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