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Mobility of ions in silicone oil

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Abstract—Data on the mobility of negative and positive ions are discussed on the basis of models developed for polymers.

Keywords —ion mobility, silicone oil, viscosity, polymers

シリコン油中のイオン移動度

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アブストラクト

シリコン油中の負イオン、正イオンの移動度のデータを高分子に対して展開されたモデルに基づいて論ずる。

キーワード — イオン移動度、シリコン油、粘度、高分子

I. Introduction

The mobility of ions in non-polar dielectric liquids has been measured and discussed for many decades. Data obtained for liquefied rare gases have received continuing interest. Although these are simple atomic liquids and the ions are of similar sizes a detailed theoretical description of transport processes is a challenging task. Another class of liquids, which have received much attention are liquid hydrocarbons, especially n-alkanes. They were studied as models for mineral oils used in the electrical industry. More recently silicone oils have been used as insulants and coolants in railway transformers and many studies

on their electrical properties have been published. In spite of this, data on the mobility of ions in silicone oil are scarce. We have recently summarized the data available so far [1].

From a theoretical point of view mobility data are usually discussed on the basis of the Stokes'-Einstein formula, which correlates the mobility with the viscosity of the liquid and the radius of the ions. A consequence is Walden's rule, which states that the product of mobility and viscosity is constant:

$$\mu_{\text{ion}} \times \eta = \text{const} \quad (1)$$

Implicit is the assumption, that the ion migrates as a single entity surrounded by a shell of polarized atoms or molecules. The viscosity of liquid hydrocarbons is of the order of 1cSt. For negative ions the data seem to follow Eq. 1, but for positive ions, Adamczewski [2] found

$$\mu_{\text{ion}} \times \eta^{3/2} = \text{const} \quad (2)$$

Silicone oils exhibit viscosities ranging from 0.65 to 10^5 to 10^6 cSt, with molecular weights starting from 162 g/mol up to 10^6 g/mol. While the low viscosity oils still exhibit a liquid character, the higher viscosity oil approach the properties of polymers.

In the present note we discuss the mobility of ions in silicone oils on the basis of theoretical concepts developed for the description of ion mobility in polymers.

II. Experimental data

The few data available in the literature concern mainly polydimethyl siloxanes. The structure formula is shown in Fig.1.

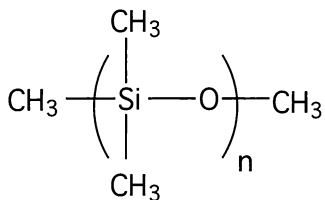
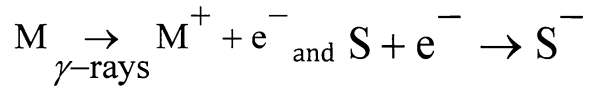


Fig.1 Structure formula of polydimethylsiloxane; n chain length

図1 ポリジメチルシロキサンの分子構造式 : nは鎖長

In most publications there is no information on what kind of negative or positive ions the measurements were carried out. Here, we concentrate our discussion on data of negative ions obtained by Holroyd and Schmidt [3], who studied the radiation induced conductivity of silicone oils and produced defined negative ions S^- by the addition of sulfur hexafluoride S,



A similar technique was employed by A. Chemin [4], who produced defined negative ions with the addition of C_7F_{14} . The data are summarized in Fig. 2 (The data of Tsuchida Fig. 2 probably refer to electrons or O_2^- , since they worked with very thin liquid layers).

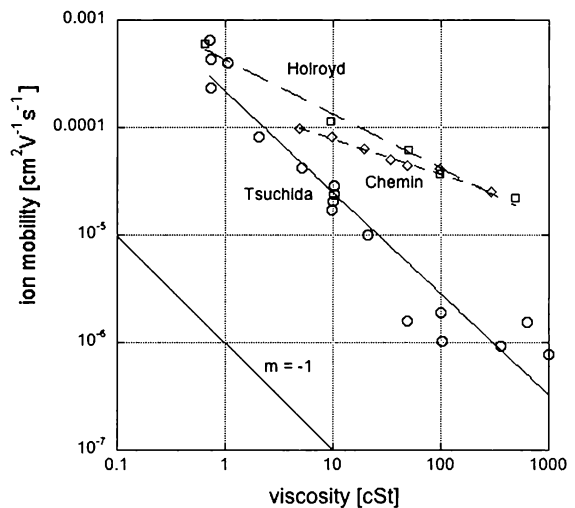


Fig. 2: Dependence of negative ions mobility in silicone oil on viscosity at room temperature

図2 : 室温でのシリコン油中の負イオン移動度の粘度依存性

Both, the data of Holroyd and Chemin for defined ions deviate from Walden's rule (Eq. 1).

In order to rationalize the data for negative ions we follow the assumptions of Mendolia and Farrington [5], who discussed the ionic mobility in macromolecular electrolytes. In polymers, where entanglement is absent, it was found that a proportionality between viscosity, η and molecular weight, M of the polymer exists,

$$\eta \propto M\zeta \quad (3)$$

ζ is the friction coefficient per monomer unit.

Silicone oil of a given viscosity usually exhibit a distribution of molecular weights. In Fig. 3 some data are shown.

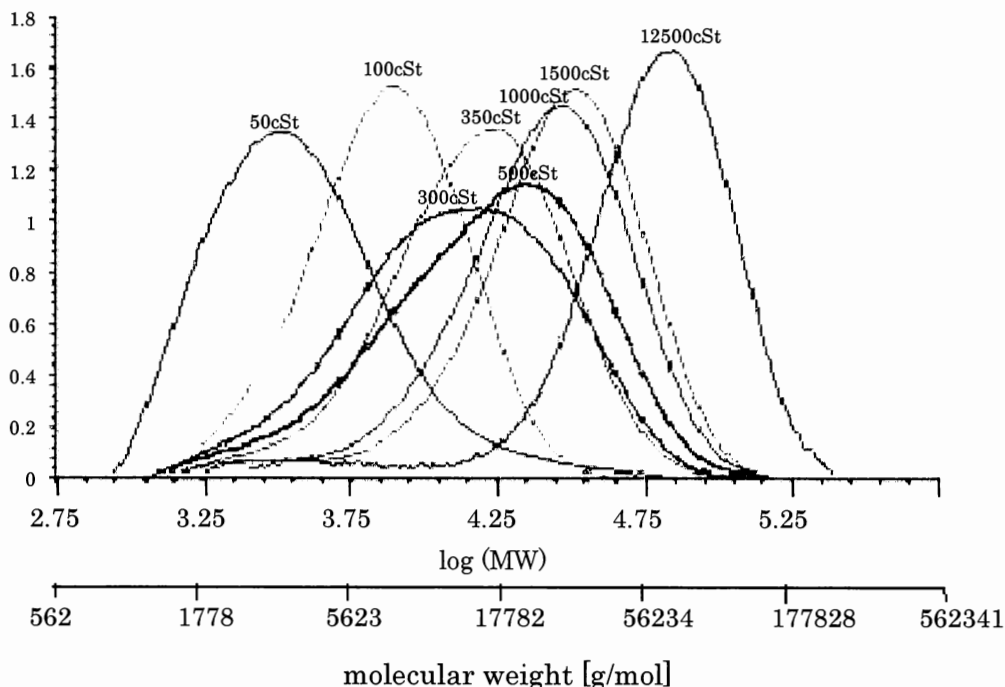


Fig.3 Molecular weight distribution of silicone oils; data taken from ref. [6]

図3 シリコン油の分子量分布；データは文献(6)から

In Fig. 4 a plot of the viscosity as a function of molecular weight is shown.

We took the data given by Wacker, which are presented in Table 1.

Table 1 molecular weight and viscosity for Wacker silicone oils [7]

表1 Wacker シリコン油の分子量と粘度

viscosity cSt	N	molecular weight
0,65	0	162
50	40	3000
100	70	5000
1000	200	15000
10000	500	37000

The viscosity is proportional to M^a with $a \geq 1$. In applying Eq. 3 to the data for SF_6^- we assume that the ions should encounter a frictional resistance closely related to the resistance, which the polymer segments feel during their thermal motion. With the assumption that the mobility varies as $1/\zeta$, the following relationship between mobility and viscosity is obtained,

$$\mu\eta \propto M^a \quad (4)$$

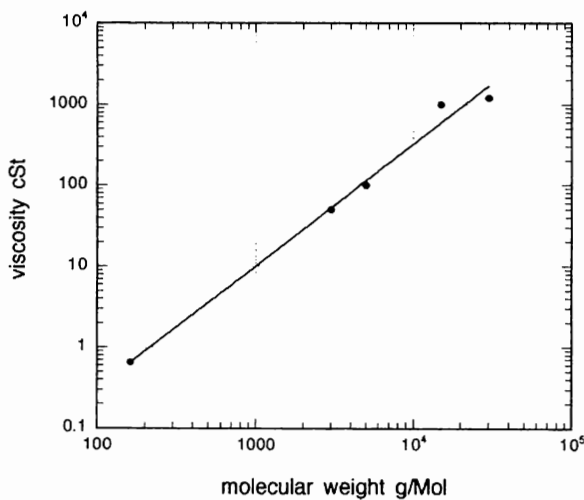


Fig.4 Correlation of molecular weight and viscosity; data of Wacker Silicones [7]

図4 分子量と粘度の相関；Wacker シリコン油のデータ

In the silicone oils entanglement is absent at lower viscosities. If we take the data of Fig 4 for M and the Holroyd-data for SF_6^- ions, the proportional relation between the product of viscosity and

mobility and the molecular weight M (Eq. 4) is obtained (see Fig. 5).

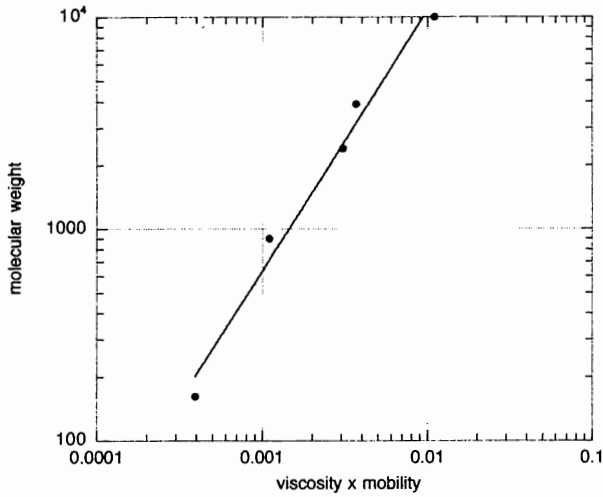
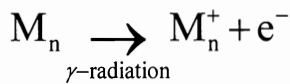


Fig. 5 Holroyd mobility data for negative ions plotted according to Eq. 4

図5 (4)式に従って描いた負イオンのホルロイド移動度データ

Positive ion mobilities are shown in Fig. 6. Here we can assume that the positive ions are macromolecules of silicone oil, which lost one electron due to ionization,



Generally, ionic transport in such case is described by a hopping mechanism, where the free volume is the determining factor. The positive charge transfers from M_n^+ to M_n by making use of an adjacent free volume. The mobility in such case is given as [8],

$$\mu_+ = \frac{e_0 d^2 \nu_0}{6k_B T} \exp\left[-\frac{V_f^*}{V_f}\right] \quad (5)$$

Where ν_0 is the attempt frequency and d is the jump distance. V_f^* is the free volume required for displacement and V_f is the mean value of the available free volume. All other symbols have the usual meaning.

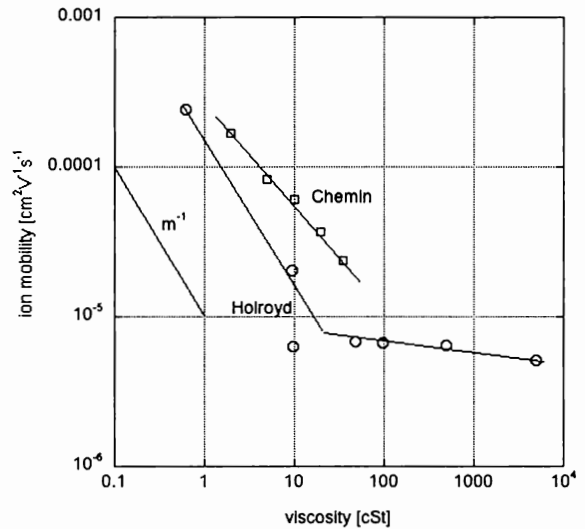


Fig. 6: Dependence of mobility of positive ions on viscosity

図6 正イオン移動度の粘度依存性

The problem of applying Eq. 5 to the case of silicone oils is that almost no data of free volumes in these oils are available. There exist only one set of data for one oil, for which the free volume had been determined from viscosity studies at various temperatures and pressures

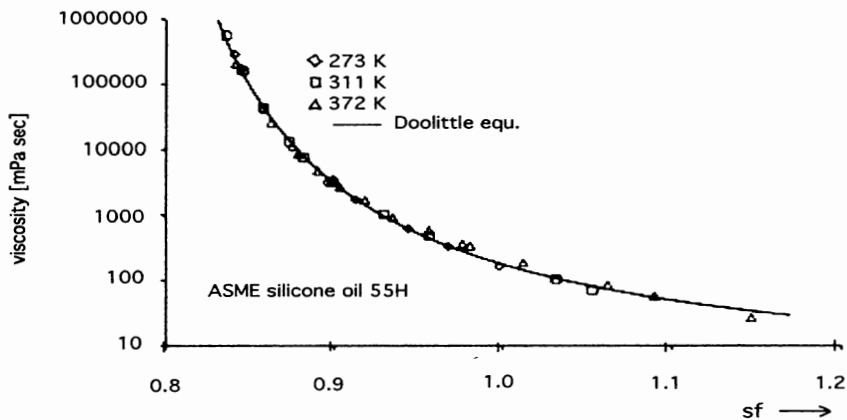


Fig.7 Master curve for viscosity as a function of free volume for ASME oil 565H [9]; the x axis is labeled sf in the following discussion.

図7 ASME オイル 565H(文献 9)に対する自由体積の関数としての粘度のマスター曲線

The x-axis is proportional to the free volume, while the y-axis shows the viscosity. The viscosity as function of free volume is given by the Doolittle equation [10],

$$\eta \propto \exp\left[\frac{B(V - V_f)}{V_f}\right] \quad (6)$$

$V - V_f$ is the volume occupied by the molecules and V_f is the free interstitial volume.

In order to rationalize the data of Fig.6 we assume that two mechanisms are active. While up to viscosities around 50 cSt, the oils behave like a liquid and the mobilities follow Walden's rule. The data of Holroyd and Chemin basically show the same dependence on viscosity, roughly $\mu \sim \eta^{-1}$. For higher viscosities the free volume model seems to be applicable. Although no data on the free volume for the oils investigated by Holroyd are available, the data of Fig. 7 give some idea on how the free volume of a specific silicone oil changes with viscosity. We take the data of Fig. 7 and calculate a hypothetical mobility factor via Eq. 5 as

$$\mu_{\text{ion}} \propto \exp\left[-\frac{1}{sf}\right] \quad (7)$$

The results are shown in Fig. 8.

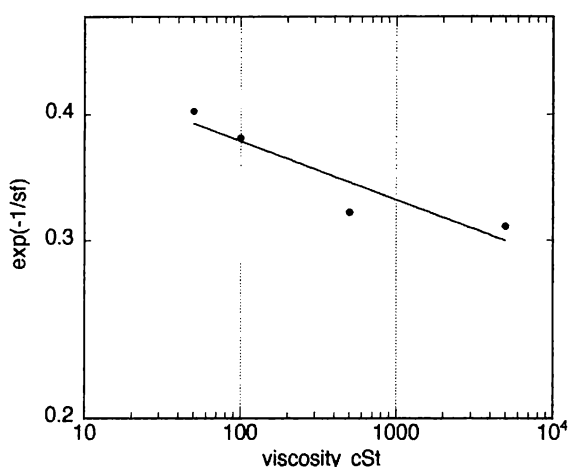


Fig.8 Mobility factor as a function of viscosity, see Eq. 7.

図8 粘度の関数としての移動度因子 (参照 式7)

The ratio of the measured mobilities $\mu(50 \text{ cSt})/\mu(5000 \text{ cSt}) = 1.3$ compares favorably with the ratio obtained from Fig. 8 of $0.4/0.31=1.29$. Generally speaking, the trend of the mobility for higher values of the viscosity can be rationalized by the free volume model.

More reliable data are required to support the discussion of the mobility of ions in silicone oils. Both models, the model for the negative ions and the model for the positive ions somehow could be combined. The present treatment seems to indicate that the models developed for polymers may be applicable for the description of the ion mobility in silicone oils.

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Werner F. Schmidt (SM 1977) received a Master's degree and Ph.D. in physics from the Free University Berlin, Germany. As a postdoctoral fellow and associate chemist, he spent three years at Brookhaven National Laboratory, New York, USA, working in areas of physical chemistry. In 1969, he entered the Hahn-Meitner-Institute, Berlin, where he initiated a research program on "excess charges in insulators." As a Privatdozent at the Free University, he supervised the Ph.D. work of 15 graduate students in physics, chemistry and electrical engineering. In 1981 and 1988 he organized international conferences on dielectric liquids, held in Berlin. He published over 250 articles in refereed journals, authored several book chapters, and edited and published several books. During his tenure at the Hahn-Meitner-Institute he spent several sabbaticals at various research institutes: 2 weeks at the Institute for High Temperatures of the former Soviet Academy of Sciences, Moscow; 3 months at IREQ (Institut de Recherche d'Hydro-Quebec) Canada; 18 months at CERN, the European High Energy Physics Laboratory in Geneva, Switzerland, where he collaborated with Carlo Rubbia and Georges Charpak on the development of radiation detectors. Twice he received the prestigious JSPS Award (Japan Society for the Promotion of Science) for stays at Osaka University (1978) and Hokkaido University (1989). He was an Invited Professor at Iwate University, Morioka (1990/91), sponsored by the Japanese Ministry of Education. He organized as director a NATO Academic Study Institute on the properties of electrons in different phases of matter (Patras, Greece, 1993). At the ICDL 1999 he was the Hans Tropper Lecturer. He acted as a consultant for Exxon-Research, New Jersey, for the Istituto Nazionale di Fisica Nucleare, Rome, Italy and for CERN, Geneva. He was guest editor of IEEE Trans. Electr. Insul. Vol. 24, No 2, 1989. Recently, he served as Editor in Chief of the Journal "Advanced Science Focus" of American Scientific Publishers.



Katsumi Yoshino was born in 1941 at Shimane, Japan. He received the B.E. degree from Department of Electrical Engineering of Osaka University in 1964. After receiving the M.E., and the Ph.D. degrees from the same University, in 1969 he became a research associate at the Department of Electrical Engineering, Faculty of Engineering, Osaka University, and in 1972 he was lecturer at the same university. From 1974 to 1975 he was a visiting scientist at the Hahn-Meitner Institute for Nuclear Research. In 1978, he was promoted to an associate professor at the same university, and in 1988 he became a professor at the Department of Electronic Engineering, Faculty of Engineering, Osaka University and retired in 2005. Presently, he is Director General of Shimane Institute for Industrial Technology, Emeritus Professor of Osaka University, Guest Professor of Shimane University, Guest Professor of Nagasaki Institute of Applied Science and Guest Professor of Osaka University. His research fields are mainly electrical and electronic materials such as conducting polymers, insulating polymers, liquids, liquid crystals, ferroelectrics, carbons, nanomaterials, superconductors, photonic crystals and displays. He published more than 1400 papers and more than 150 patents. He has received many awards and honors such as IEEE Fellow, The Japan Society of Applied Physics Fellow, The Institute of Electrical Engineers of Japan Fellow, The Institute of Electronics, Information and Communication Engineers Fellow, The Japanese Liquid Crystal Society Award, The Society of Polymer Science, Japan Award, Osaka Scientific Award etc.. He contributed to the progress of science and technology in various societies as active members such as Vice President of The Institute of Electrical Engineers of Japan and President of The Japanese Liquid Crystal Society. He organized several International Conferences such as International Conference on Dielectric Liquids in 1999 at Nara and also contributed a lot as active members of International Conferences such as organizing committee member, advisory member and executive committee member etc.



Alexey G. Khrapak was born in Moscow, Russia in 1946. He received the B.S. degree in Physics from the Physical Faculty, Moscow University in 1969, and the PhD and Dr.Sci. degrees in plasma physics from the Institute of High Temperatures, Russian Academy of Sciences, Moscow in 1975 and 1989, respectively. At present he is Head of a Laboratory and Principal Scientist at the Joint Institute for High temperatures, Russian Academy of Sciences, in Moscow. He is author of three monographs, eight review papers and about 100 publications in refereed Journals. He was a guest scientist at Hahn-Meitner-Institute Berlin, Hokkaido University Sapporo and Osaka University, Osaka. At present he has a continuing cooperation with the Max Planck Institute for Extraterrestrial Physics, Munich, Germany.