THE TEMPERATURE DEPENDENCE OF ELECTRIC CONDUCTANCE OF POLAR LIQUID DIELECTRICS

By

L. HORVÁTH

Technical High School, Subotica, Yugoslavia

Continuous measurements were performed for conductivity and permittivity of some polar liquid dielectrics in the wide temperature range from the melting to the critical point in a closed measuring cell under saturated vapor pressure of their own. The measurements were made on methyl alcohol, ethyl alcohol, acetone and sulphur dioxide at a frequency of 1591.5 Hz.

Introduction

The electric conductance of pure liquid polar dielectrics, which arises from autodissociation of their molecules, depends to a great extent on temperature, due to its influence on the number of ions, their mobility and some physical characteristics of liquids. The electric conductance of sufficiently purified polar liquid dielectrics whose dielectric constant is relatively high, can be considered as a characteristic constant liquids. The electric conductance of sufficiently purified polar liquid dielectrics whose dielectric constant is relatively high, can be considered as a characteristic constant of the substance.

In this work electric conductance measurement has been carried out from the melting temperature to the critical temperature, *i.e.* in the temperature interval in which the liquids can exist under saturated vapor pressure. The measurements were carried out on methyl alcohol, ethyl alcohol, acetone and sulphur dioxide. Data on electric conductivity of these substances can be found in the literature by various authors [1—9], but they dealt with particular temperatures or temperature ranges only and the purity of used substances, for the most of these measurements, can be questioned. We want to make perfectly clear the importance of the possibility of simultaneously measuring the conductivity and permittivity and we think that a continuous measurement of these data will give us more reliable values than separate measurements.

Experimental technique

The conductivity and permittivity were measured by means of a bridge method. The capacity and the conductance of the condenser were measured with a Wayne—Kerr B 331 Mk II Autobalance Precision Bridge, at the frequency 1591.5 Hz ($\omega = 10^4$ 1/s).

The measurement range of the bridge for capacity is from 100 aF to 1 F and for conductivity from 1 pS to 10 kS. The bridge error was 0.01 %. The bridge enables simultaneous measurement of resistance as well as capacity.

For the continuous regulation of temperature in the interval of $-80\,°C$ $- +180\,°C$ the "Materialprüfkammer" type VMT II from Vötsch was used. The temperature above 180 °C was achieved in an oil bath, while under $-80\,°C$ in a dish recooled by liquid oxygen. The temperature measurement was carried out by means of a copper-constantan thermocouple. The error in temperature determination was estimated at 0.1 °C [10, 11].
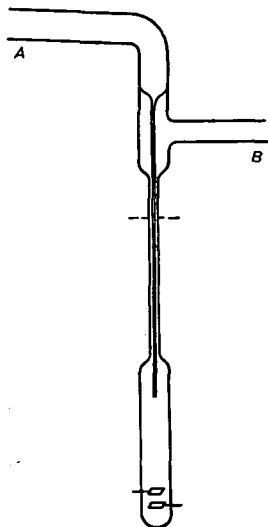

Fig. 1. The measuring cell

The measuring cell used in the experiment, made of Pyrex glass, is presented in Fig. 1. The cell was at part A connected to the reservoir filled with the purfied substance, while at part B it was connected to the recipient which could be evacuated. The investigated substance was introduced into the cell in gaseous state, where it was transformed into liquid state by intensive recooling. The cell was filled to the volume, which corresponds to the critical volume of the investigated substance. After filling the cell was melted with flame and closed at the indicated line and separated from its upper part, while the lower part was cooled and protected by an asbestos card-board. The cell was calibrated by the method which is recommended in the literature [12, 13]. Each cell was examined before measurement in the temperature interval in which it was used, with air as dielectric. The change of cell capacity, obtained by this measurement, enabled a certain error correction which appears due to thermic deformation.

To obtain pure methyl alcohol, ethyl alcohol and acetone the deionisation method and the fractional vacuum distillation were used. This way a substance of very low conductivity was obtained [14, 15]. Sulphur dioxide was obtained and purified by the method recommended in the literature [16]. Before measurement in the cell five fractional vacuum distillations were carried out, using the middle fraction only till constant conductivity was achieved.

Result

The measured conductivity values as a function of temperature are given in Table I and Fig. 2. Table I contains the average of three measurements. The error was at about 5 % at low and high temperatures, room temperature it was under 2 %.

The permittivity *vs.* temperature curves can be fitted with the following third order power laws:

for methyl alcohol $\varepsilon_{(T)} = 1.99 \cdot 10^2 - 1.17T + 2.79 \cdot 10^{-3}T^2 - 2.45 \cdot 10^{-6}T^3$

for ethyl alcohol $\varepsilon_{(T)} = 1.34 \cdot 10^2 - 7.08 \cdot 10^{-1}T + 1.50 \cdot 10^{-3}T^2 - 1.19 \cdot 10^{-6}T^3$

for acetone $\varepsilon_{(T)} = 58.3 - 1.40 \cdot 10^{-1}T + 5.39 \cdot 10^{-5}T^2 + 9.42 \cdot 10^{-8}T^3$

for sulphur dioxide $\varepsilon_{(T)} = 88.5 - 5.14 \cdot 10^{-1}T + 1.20 \cdot 10^{-3}T^2 - 1.08 \cdot 10^{-6}T^3$
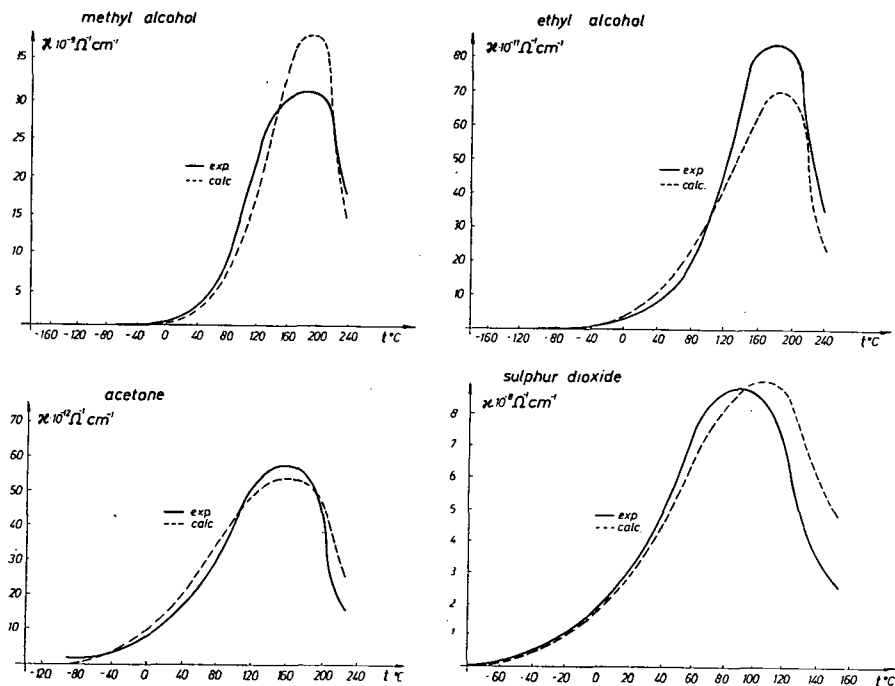

Fig. 2. Conductivity of methyl alcohol, ethyl alcohol, acetone
and sulphur dioxide as a function of temperature

The conductivity maximum appears for methyl alcohol at about 195 °C, for ethyl alcohol at about 190 °C, for acetone at about 162 °C, and for sulphur dioxide at about 93 °C. The maxima are in the same areas, if they are expressed by the reduced temperature $T_r = T/T_c$, where T_r is a reduced temperature, and T_c is the critical temperature. The reduced temperature of the maximum for methyl alcohol is 0.91, for ethyl alcohol 0.90, for acetone 0.85 and for sulphur dioxide 0.85. The transition into gaseous state is not followed by a jump either in electric conductivity or permittivity.

Table 1

Conductivity of methyl alcohol, ethyl alcohol, acetone and sulphur dioxide as a function of temperature

t°C	Methyl alcohol $x \cdot 10^{-1}\Omega^{1-}cm^{-1}$	Ethyl alcohol $x \cdot 10^{-10}\Omega^{-1}cm^{-1}$	Acetone $x \cdot 10^{-12}\Omega^{-1}cm^{-1}$	Sulphur dioxide $x \cdot 10^{-1}\Omega^{-1}cm^{-1}$
−110	—	0.11	—	—
−100	—	0.14	—	—
−90	0.057	—	1.30	—
−80	0.068	0.24	1.72	—
−70	—	—	—	0.13
−60	0.11	0.42	2.54	0.19
−40	0.18	0.77	3.19	0.49
−20	0.29	1.31	5.22	0.99
0	0.51	2.21	7.35	1.87
20	1.12	3.87	11.2	2.90
40	2.25	6.87	15.3	4.82
60	5.01	11.3	21.1	7.60
80	8.63	18.6	29.2	9.08
100	15.2	31.1	39.1	8.82
120	22.1	47.2	49.8	7.63
130	—	—	—	5.09
140	27.7	67.4	55.1	3.80
150	—	—	—	2.94
160	30.2	81.0	56.8	2.54
180	30.9	85.3	54.9	—
200	31.0	84.1	48.2	—
210	—	—	37.3	—
220	28.7	58.8	19.3	—
230	21.8	46.7	15.1	—
240	18.1	35.4	—	—

Discussion

In the result analysis we have started form the liquid model which supposes a molecule arrangement on the short distances. In such a liquid due to the action of dipoles strong local fields appear and in the potential field of this type the movement of dipoles and of ions formed by autodissociations was quite limited. Started from this model [17—21], the quantitative expression for conductivity can be found,

$$\varkappa = \frac{c_o Z^2 e^2 \Delta l^2 \bar{v}}{6kT} \exp\left\{-\frac{U_o}{RT}\right\}, \tag{1}$$

where $\varkappa$ is the conductivity, c_o — the concentration of ions, e — the elementary charge, Δl — the medium distance value between two next free places for the movement of ions, $\bar{v}$ — the medium frequency value of a breaking out attempt of a potential barrier, k — Boltzmann constant, U_o — the activation energy of process, and T — the thermodynamic temperature.

For the smaller temperature interval, neglecting the change of the preexponential terms in relation to the exponential term, we obtain

$$\varkappa = A \exp\left\{-\frac{U_o}{RT}\right\} \tag{2}$$

This equation has often been proposed as an expression describing the temperature dependence of the conductivity. Using the experimental data we tried to bring the physical values in equation (1) to a qualitative connection with the values which we measured. The average ion speed, approximately equal to the average molecule speed, can be expressed as

$$\bar{v} = \frac{\Delta l}{\Delta t} \tag{3}$$

where Δt is the time travelling of distance Δl. Substituting $l/\Delta t$ with the frequency of jump attempt of the potential barrier, we have

$$\bar{v} = \bar{v}\Delta l \text{ respectively } \bar{v}\Delta l = \bar{v}\Delta l^2 \tag{4}$$

With decreasing density the number of free spaces increases reducing there by the distance between next free spaces, while the average speed is proportional to the root of thermodynamic temperature:

$$\bar{v}\Delta l^2 = \varrho\sqrt{T} \tag{5}$$

The ion concentration is proportional to the concentration of the nondissociated molecules, *i.e.* to the density and to the dissociation degree. In the first approximation it can be assumed that dissociation degree will be proportional to the permittivity as a factor determining the Coulomb interaction force. The change of thermal energy will influence the degree of dissociation as a direct cause of dissociation, while the energy is proportional to the thermodynamic temperature. The ion concentration could be connected to the values in the simplest from:

$$c_o = \frac{N}{M}\varrho\alpha = \frac{N}{M}\varrho\varepsilon T \tag{6}$$

Eq. (1) can consequently be expressed as

$$\varkappa = \frac{Z^2 e^2 N p\varepsilon T\varrho\sqrt{T}}{6kTM} \exp\left\{\frac{U_o}{RT}\right\} \tag{7}$$

or in more condensed form

$$\varkappa = K\varepsilon\varrho^2\sqrt{T} \exp\left\{-\frac{U_o}{RT}\right\} \tag{8}$$

The constant K contains the physical quantities which do not change with temperature and proportionality factois. Using the permittivity data in the whole temperature interval and the available data on density from the temperature interval and the available data on density from the literature [22—27], the calculated results were presented according to Eq. (8). The reproducibility of the course of the experimental curve can be satisfactory, taking into consideration the semi-quantitative character of Eq. (8). The application of Eq. (8) for the determination of the conductivity of water, for which we have the experimental data [27—30] on conductivity, density and permittivity, gave us similar results. Eq. (8) predicts the maximum of conductivity of water on the temperature cca. 270 °C, what is an agreement with some experimental data and with the course of experimental curve. The reduced temperature of the maximum of water is 0.84, expressed according to the Eq. (8).

Conclusions

The experimental results show that the conductivity of the investigated substances as a function of temperature goes through a maximum. Observations point out that this is a general feature of all polar liquid dielectrics. We consider that the cause of the decreasing conductivity is the declining number of ions at higher temperatures and the suddenly declining density approaching the critical temperature. The thermal energy as a direct cause of dissociation increases more slowly than the above mentioned factors decrease in this temperature interval causing a maximum in $x = f(t)$.

References

[1] *Evers, E. C., A. G. Knox:* J. Am. Chem. Soc. **73**, 1739 (1951).
[2] *van Dyke, R. E.:* J. Am. Chem. Soc. **72**, 2823 (1950).
[3] *Cady, H. P., R. Taft:* J. Phys Chem. **29**, 1075 (1925).
[4] *Walden, P.:* Das Leitvermögen der Lösungen (Akademische Verlagsgesellschaft m.b.H. Leipzig, 1924).
[5] *Landolt—Börnstein:* Zahlenwerte und Funktionen (Springer Verlag, Berlin Göttingen—Heidelberg, 1964).
[6] *Briere, G.:* Ann. Phys. **9**, 73 (1964).
[7] *Barret, S., G. Briere , N. Felici, G. Pierre:* C. R. Acad. Sc. Paris, 4400—4403 (1965).
[8] Ullmanns Encyklopedie der technischen Chemie, III Auflage, Urban   Schwarzenberg, Berlin (1960).
[9] *Dannhauser, W.:* J. phys. Chem **68**, 2007;(1964).
[10] *Dulić, N. ,L. Horváth:* Acta Phys. et Chem. Szeged, **4**, 451 (1978).
[11] *Dulić, N., L. Horváth:* Bulletin de la société chimique Beograd **45** 358 (1980).
[12] *Kohlrausch, F.:* Praktische Physik (Teubner Verlagsgesellschaft, Stutgart, 1955).
[13] *Mecke, R., R. Joeckle, G. Klingenberg:* Z. für Elektrochemie, **66**, 239 (1962).
[14] *Felici, N. J.:* Brit. J. Appl. Phys. **15**, 801 (1964).
[15] *Inczédy, J.:* Ioncserélők analitikai alkalmazása (Műszaki Könyvkiadó, Budapest, 1962).
[16] *Müller G., G. Gnauck:* Reinste Gase (VEB Deutscher Verlag der Wissenschaften, Berlin, 1965).
[17] *Frenkel J.:* Kinetic Theory of Liquids (Clarendon Press, Oxford, 1946).
[18] *Szkanavi, I. G.:* Dielektrikumok fizikája (Akadémiai Kiadó, Budapest, 1953).
[19] *Hirschfelder, J. O., C. F., Curtiss, R. B. Brid:* Molecular Theory of Gases and Liquids (J. Wiley et Sons, Inc. New York, 1964).
[20] *Fröhlich, H.:* Theory of Dielectrics (Clarendon Press, Oxford, 1968).
[21] *Rost, A.:* Messungen dielektrischer Stoffeigenschaften, (Viewege, Braunschweig, 1978).
[22] *Young, S.:* Sci. Proc. Roy. Soc. Dublin N. S. XII. 374 (1909—10).

[23] *Lange, A.:* Z. angew. Chem. 275, (1899).
[24] *Herz, A., E. Neukrich:* Z. Phys. Chem. **104**, 433 (1923).
[25] *Cardoso, E., E. Sorrentino:* J. Chim. Phys. **24**, 77 (1927).
[26] *Brewer A. D., J. E. C. Hutchins:* Nature, London, **210**, 1257 (1966).
[27] *Wright, J. M. jun., W. T. Lindsay, T. R. Druga:* WAPD—TM—204 U.S.A.C. (June 1961).
[28] *Wilde, B. E.:* Electrochimica Acta, **12**, 737 (1967).
[29] *Akerlof, G. C., H. J. Oshry:* J. Am. Chem. Soc. **72**, 2844 (1950).
[30] *Fairbrother, F.:* J. Chem. Soc. 1051 (1948).

ТЕМПЕРАТУРНАЯ ЗАВИСИМОСТЬ ЭЛЕКТРИЧЕСКОЙ ПРОВОДИМОСТИ ЖИДКИХ ПОЛЯРНЫХ ДИЭЛЕКТРИКОВ

Л. Хорват

Проведены непрерывные измерения проводимости и диэлектрической проницаемости некоторых жидких полярных диэлектриков, в широком температурном интервале от точки плавления до критической точки, в закрытой измерительной ячейке при давлении насыщенных паров. Измерения проводились метиловым и этиловым спиртами, ацетоном и двуокисью серы при частоте 1591,1 Гц.