NOTATION

τ, time; λ, thermal conductivity; b, b_P, b_T, rates of change of temperatures of block, plate, and working layer of heat meter; C_{BL}, C_P, C_T, total heat capacities of block, plate, and working layer of heat meter; S, h, cross-sectional area and thickness of sample; k_T, thermal conductivity of heat meter; N_T, N_{samp}, instrument readings in measurement of heat-meter signal and temperature drop across sample; σ_T, σ_r, thermal conductivities from lateral surfaces of sample to end and radial surfaces of annular sublayer; R_1, R_2, radii of sample and block; $\bar{t}_{samp}$, $\bar{t}_{BL}$, average temperatures of sample and blocks; $\varepsilon = \pi l$ (l = 1, 2, 3, ...); δ_{adm}, admissible error of measurement.

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DETERMINATION OF LIQUID SOLIDIFICATION PRESSURE BY MEASUREMENT OF DIELECTRIC LOSSES

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UDC 531.787

A method is described for determining solidification pressure p_s of a liquid by measuring its low-frequency dielectric losses; experimental p_s values are presented.

The problem of determining liquid solidification pressures arises from the need to protect components of high-pressure apparatuses from injury due to solidification of the working liquid or liquid being studied. This is especially important in the operation of fragile components of precision apparatuses such as high-pressure viscosimeter measurement cells, bellows piezometers, resistance manometer coils, etc., and in establishing the operating characteristics of new working fluids. This question is also of great practical importance in several branches of industry (lubricant production, hydroextrusion, etc.).

In the great majority of cases the transformation of a liquid into a solid state occurs more or less gradually and is characterized by the formation of an amorphous glass. The abrupt crystallization of metals at a fixed pressure and temperature is probably only an extremal case of the more universal phenomenon of vitrification. In vitrification the liquid viscosity gradually becomes so high that formation of a crystalline lattice is impossible due to the low mobility of molecules or atoms. Vitrification is often observed at high pressures, since the viscosity of many liquids increases by several orders under such conditions. Thus, liquid solidification at high pressure extends over a certain pressure interval for any given fixed temperature.

At present there exists no generally accepted criterion defining the completion of the transformation of the liquid phase to solid. It is probably most expedient to relate the degree of solidification of a substance to its viscosity. For example, Turnball [1] proposes that a substance be considered solidified when its viscosity exceeds 10^{14} Pa · sec. But with this criterion, tin at room temperature is not

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Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 29, No. 4, pp. 620-623, October, 1975. Original article submitted October 23, 1972.

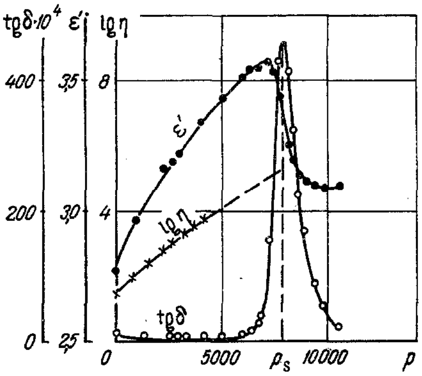

Fig. 1

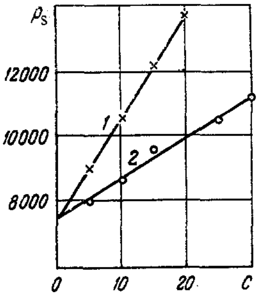

Fig. 2

Fig. 1. Dielectric loss-angle tangent tan δ dielectric permittivity ε', and log viscosity log η versus pressure p, 10^5 Pa, for silicone polymethylsiloxane liquid PMS-2500 at 20°C. ν = 800 Hz, t = 20°C.

Fig. 2. Solidification pressure of PMS-2500 liquid dissolved in n-heptane (1) and toluol (2) versus solvent concentration at t = 20°C; p_s, 10^5 Pa; C, solvent concentration by wt. %.

solid, since its viscosity is $2 \cdot 10^{12}$ Pa · sec. Thus for many practical purposes a material must be considered solid at viscosities significantly lower than required by the Turnball criterion. Direct methods of liquid viscosity measurement, for example, the falling-sphere method, are not applicable in determining the moment of solidification, since the upper limit of sphere viscosimeter measurement is 10^3 Pa · sec.

The present authors have developed a simple method of determining solidification pressure based on measurement of dielectric losses.

As is well known [2], dielectric relaxation time in liquids is approximately proportional to viscosity, and thus should increase with increase in pressure. When the dielectric relaxation time τ becomes equal to the reciprocal of the circular field frequency ($1/\omega$) relaxation absorption of the electromagnetic field energy becomes maximal, i.e., the dielectric loss factor ε'' reaches a maximum. Thus the function $\varepsilon''(p)$ has a maximum $\varepsilon''_{\max}$ at $p = p_s$; p_s, the pressure at which the dielectric relaxation time $\tau = 1/\omega$.

Figure 1 presents experimental data on the baric dependence of ε', log η, and tan δ for the polymethylsiloxane PMS-2500 [GOST (All-Union State Standard) 13032-67]. Measurements were performed at a frequency of 800 Hz. Near a pressure of $8000 \cdot 10^5$ Pa there is a sharp maximum in dielectric loss. The dielectric permittivity ε' in this region drops by approximately 15%. This is because at such pressures the liquid viscosity becomes so high that the orientation component of the polarization caused by molecular motion does not contribute to the total polarization. Extrapolation of the function log $\eta(p)$ (crosses in the figure indicate experimental results) to a pressure of $8000 \cdot 10^5$ Pa gives a value of 10^4-10^5 Pa · sec.

It has been experimentally established that at $\eta \geqslant 10^4$ Pa · sec bellows piezometers and viscosimeter measurement cells cease to function, while manganin manometers lose their sensitivity due to the appearance of shear stresses upon liquid vitrification. Thus in working with fragile high-pressure precision apparatuses a viscosity of $\eta = 10^4$ Pa · sec may be regarded as the limit for the working fluid. At higher pressures the material must be considered solid.

Table 1 presents the results of solidification-pressure measurements for some liquids at various temperatures, while Fig. 2 shows solidification pressures of solutions of PMS-2500 in n-heptane and toluol as functions of solvent concentration by weight. For the dielectric loss measurements a quite simple capacitance cell of the high-pressure type, described in [3], was used with a Tesla VM 400 precision bridge (ν = 800 Hz).

TABLE 1. Liquid Solidification Pressures (by dielectric loss measurement; t, °C; p, 10^5 Pa).

Liquid	t	p_s	t	p_s	t	p_s
Oil MS-20 (GOST 1013-49)	21,6	2600	110	9200	150	13200
Spindle oil (GOST 1707-51) – 50% kerosene (GOST 4753-68)	16,8	10200				
Cylinder oil (GOST 6411-52)	21,0	2400	80,6	6400	109	8100
Polymethylsiloxanes (GOST 13032-67):						
PMS-1,5	20,0	10800				
PMS-100	25	8600	95,5	14500	105	>15000
PMS-2500	20	7600	80,7	12000	121,1	>15000
Polyethylsiloxanes						
PES 5 (GOST 13004-67)	20,0	>15000				
PES-S-2 (GOST 10957-64)	20,0	>15000				

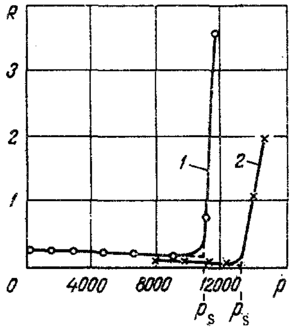

Fig. 3. Electrical resistance of water emulsion versus pressure (relative units) at 20 (1) and 40°C (2).

The proposed method of determining solidification pressure is applicable only to polar liquids in which the orientation contribution to total polarization is nonzero. However, in some cases the method can be extended to nonpolar liquids. To do this it is necessary to add a slight quantity of a polar impurity to the nonpolar liquid. A small amount of such an impurity has practically no effect on solidification pressure.

In conclusion, we will note a modification of the method, the limiting case where $\omega \to 0$. In fact, measurement of the dc electrical resistance of the material allows evaluation of the degree of transformation to the solid state. As was shown in [4] the dependence of the logarithm of electrical conductivity on log of viscosity $\log \gamma = f(\log \eta)$ coincides with the function $\log \tau = f(\log \eta)$. Determination of the solidification pressure by electrical-resistance measurement gives best results for crystallizing liquids. In this case a rapid growth of resistance is observed over a narrow pressure range, which corresponds to the solidification pressure. An example of such a liquid is a water emulsion (water concentration 98%). The function $R = f(p)$ for temperatures of 20 and 40°C is shown in Fig. 3.

NOTATION

τ, dielectric relaxation time; ω, circular frequency of external electromagnetic field; ν, electromagnetic field frequency; ε', dielectric permittivity; ε'', dielectric loss factor; $\tan\delta$, dielectric loss-angle tangent; η, viscosity; p, pressure; p_s, solidification pressure.

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