Properties of Superheated Liquids

Viscosity of Carbon Tetrachloride

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A capillary tube viscometer has been developed which enables study of viscous shear in Newtonian liquids under superheated conditions. The viscosity of CCl_4 near atmospheric pressure is reported for superheats as high as 38.1° C. Although the results agree favorably with those obtained by Titani under subsaturated conditions, the effect of pressure is much larger than that obtained by extrapolating the Bridgeman high pressure data.

IN A previous paper (*3*), an experimental method for investigating the superheated liquid state was described, and results of a *PVT* study of CCl_4 were reported which are in accordance with published data for CCl_4 under subsaturated conditions. However, there is no assurance that transport phenomena in superheated liquids should demonstrate a comparable accord, because theories for irreversible processes contain, of necessity, some sort of mechanism for relaxing the nonuniform state which may well be influenced by metastable considerations. The purpose here is to report an experimental method for studying the behavior of superheated liquids undergoing shear, and to establish the effect of pressure and temperature on the viscosity of superheated CCl_4.

APPARATUS AND PROCEDURE

A schematic diagram of the over-all apparatus appears in Figure 1. Principal functional sections include a high vacuum system, *HVS*, Hg and CCl_4 degassers, *MD* and *LD*, Torricellian barometers, *TB1*, *TB2*, and *TB3*, a capillary tube viscometer, *CV*, and a metering buret, *MB*. Details of *CV* appear in Figure 2, where the glass envelope enclosing the capillary tube, *CT* (radius = 0.0137 cm., length = 28.966 cm.), and adjoining inlet and exit sections, *IS* and *ES*, functioned as a constant temperature bath. Temperature was controlled by means of film condensation of steam generated in the reboiler, *RB*, whose heat input was governed by an electronic controller, which was activated by differential changes in *TB2* mercury level using capacitance type sensors, *C2*. Dimensions of *IS* and *ES* were established from the Graetz solution (*6*) to ensure that the temperature in *CT* was uniform. Inlet and exit temperatures in *CV* were monitored with iron-constantan thermocouples cemented in place in *IW* and *EW* as shown. The viscometer was oriented vertically so that gravity would provide the principal driving force for flow. (Since the local superheat of an element of fluid traversing *CT* depended on the local hydrostatic pressure, a uniform superheat would have required that $\partial P/\partial Z = 0$.) Inlet and exit pressures to *CT* were established by controlling the vapor pressure of CCl_4 stored in *LR* and by pressurizing with pure N_2 the ballast tank, *BT*. Using the above procedures, it was possible (with care) to control the temperature in *CV* and the pressure drop across *CT* to within 0.05° C. and 0.1 mm. of Hg, respectively.

The experimental program was begun by assembling the apparatus as shown in Figure 1, using one-shot glass break-out valves (*V1*, *V2*–not shown, and *V3*) to separate service sections, *LD*, *MD*, and *MB*, from the viscometer. Internal surfaces of the all-glass apparatus then were degassed by raising their temperature to 400° C. under a high vacuum of 10^{-7} mm. of Hg. This condition was maintained for approximately 10 days, during which time triple-distilled Hg and spectroscopic grade CCl_4 were charged to *MB* and *LD*. [Detailed descriptions of the techniques used to degas the mercury charged to *TB1* and the CCl_4 charged to *LR* and *CV* are available (*4*).]

After the liquids had been degassed, they were charged in vacuo to *TB1* and *LR* by performing, in order, the following steps: seal glass line to *HVS* at *S4*, open *V2* (located to left of *S1*), seal glass line at *S1*, open *V1*, seal glass line at *S5*. With the removal of service sections *HVS*, *MD*, and *LD*, the remaining apparatus (enclosed in dashed lines in Figure 1), which was mounted on a massive platform supported by shock mounts, was immune to mechanical shock.

At this stage, CCl_4 in *CV* was separated from N_2 in *MB* by the glass diaphragm in *V3*. After desired conditions were established, *V3* was opened and liquid effluent entered *MB* along a thin vertical wire which was stationed in the center of the buret to give a quiescent interface. Data for calculating volumetric flow rates in *CT* were obtained by measuring the rate of rise of the meniscus in *MB*, with a cathetometer and stopwatch, recording the times for successive 1-cm. rises until steady state occurred. After the first run, flow to the buret was interrupted (and initiated) by freezing (and then melting) the CCl_4 contained in the capillary freeze valve, *CFV*.

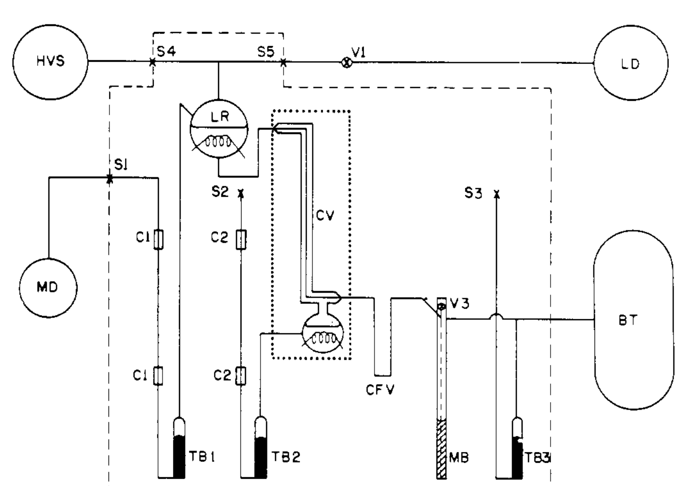

Figure 1. Schematic diagram of apparatus

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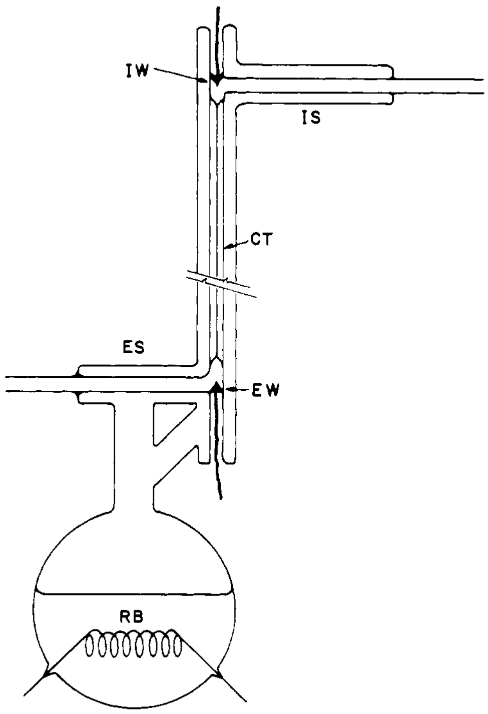

Figure 2. Capillary tube viscometer

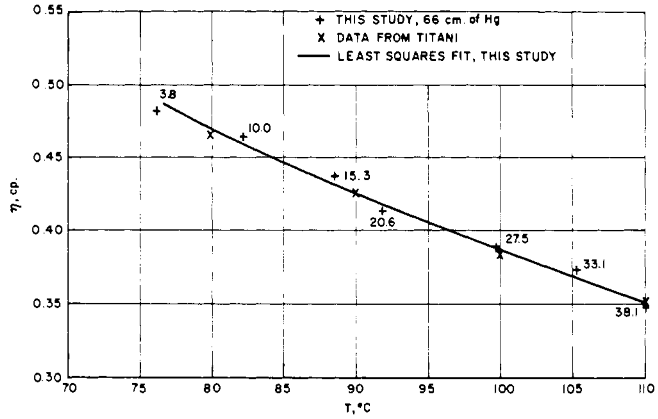

Figure 3. Viscosity *vs.* temperature

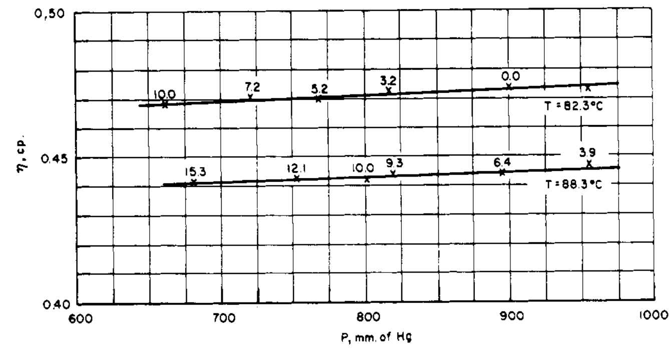

Figure 4. Viscosity *vs.* pressure, superheated conditions

CALCULATIONS

The coefficient of viscosity was calculated from the Hagen-Poiseuille expression (*1*). Geometries of *CT* and *MB* were measured according to a technique described by Giddings (*5*). (The effect of pressure and temperature on these dimensions was negligible.) Calculated values of flow rates and effective driving forces in *CV* included the effect of temperature and pressure on the densities of Hg and CCl_4 in the various sections of the apparatus. A correction was applied for end effects (*5*), using measured values of inlet and exit geometries to *CT*. Scatter in the results is due primarily to difficulties encountered in controlling the upstream pressure in *CV*. (Although the pressure drop across *CT* was controlled to within 0.1 mm. of Hg, the over-all driving force across *CT* was restricted to about 10 mm. of Hg owing to the requirement that $\partial P/\partial Z$ be small.)

Superheats were calculated by taking the difference between the temperature as measured in *CV* and the saturation temperature corresponding to the average pressure in *CT*. The maximum error in these values is 0.2° C. with negligible variation along *CT*.

RESULTS AND DISCUSSION

The data were taken in two ways. In one series of runs, the superheated state was entered by raising the temperature in *CT* at constant pressure. Typical results appear in Figure 3, where the subsaturated (but pressurized) data of Titani (*7*) have been added for comparison. If the Titani data are corrected to 66 cm. of Hg (using Bridgeman's log η *vs.* P results (*2*) near $P = 1$ atm. to obtain $\partial\eta/\partial P$), the two studies are in sufficiently close agreement to conclude that the effect of superheating on η is small.

In a second series of runs, the superheated state was entered by reducing the pressure in *CT* at constant temperature. Typical results appear in Figure 4, where the extent of superheating is indicated as in Figure 3. The solid lines are linear least-squares fits to the data whose slopes give $(\partial\eta/\partial P)_T$. These slopes are to be compared with values calculated from the Bridgeman isotherms near atmospheric pressure:

T, ° C.	$(\partial\eta/\partial P)_T \times 10^5$, cp./mm. of Hg	
30	0.108	Bridgeman
75	0.065	
82.3	1.7 ± 0.6	This study
88.3	1.4 ± 0.5	

Apparently the viscosity of CCl_4 under superheated conditions is much more sensitive to pressure than would be expected from an extrapolation of existing (subsaturated) data. Although the confidence limits on the slopes are far from excellent, they provide insufficient grounds for omitting the results. Furthermore, the authors have re-examined every possible source for error which would contribute to a systematic bias of the data. None could be found, and in an effort to resolve the matter the apparatus is being redesigned to extend the pressure range and to improve the accuracy of the results.

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