Purification of silicone oils for fluid experiments

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Abstract Commercially produced silicone oils (polydimethylsiloxanes or PDMS) that are used in many fluid experiments typically contain a mixture of linear polymers with a distribution of molecular weights. This multicomponent constitution can cause undesirable effects in some experiments; we show one such effect in surface-tension-driven Bénard convection. We describe a simple distillation protocol for obtaining low viscosity single-component silicone oils from commercially available mixtures. For polymers with molecular weights ~ 1000, our method yields purities of better than 95 %.

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Introduction

In fluid mechanics, the term "silicone oils" frequently refers to liquid organosilicon polymers more properly known as polydimethylsiloxanes (PDMS) that have long been employed in a wide variety of experiments (see, e.g., Koschmieder 1967; LeGal et al. 1985; Kamotani et al. 1992; Marsh et al. 1993). PDMS are frequently selected because they are available in a wide range of viscosities and possess the important advantages of chemical inertness, transparency, and non-toxicity (McGregor 1954). PDMS are especially valued in studies of phenomena involving liquid-gas or liquid-liquid interfaces (e.g., moving contact lines, surface-tension-driven flows). Such experiments can be quite sensitive to small amounts of uncontrolled contaminants at the interface (Berg and Acrivos 1965); the very low surface energy of PDMS resists these effects.

PDMS typically used in fluid experiments suffer from the disadvantage that they are not pure (i.e., monomolecular) liquids but are mixtures of linear polymer chains that share the

characteristic chemical composition

$$(CH_3)_3 SiO [SiO (CH_3)_2]_n Si(CH_3)_3. \tag{1}$$
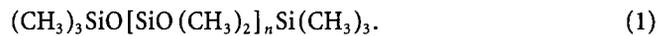
where n varies over some range. For example, 10 centistokes (cS) Dow Corning 200® silicone oil possesses a mean molecular weight of 1100 with a standard deviation of 470 (Dow 1994). Thus, the 10 cS oil contains a large number of different polymer lengths since the molecular weight for a chain of length n is $(74n + 102)$. Figure 1 illustrates some of the polymers in the 10 cS oil. Since PDMS are formed in polymerization reactions (McGregor 1954), the range of n is indirectly controlled by selecting the viscosity of the mixture through adjustment of process control parameters such as temperature, pressure, and amount of catalyst. Physical properties can vary (e.g., the viscosity of 5 cS Dow Corning 200® silicone oils is specified to $\pm 10\%$, according to a Dow Corning Corp. Certificate of Analysis) because the relative concentrations of the polymers in the mixture can change from lot to lot in commercial production. Thus, use of PDMS in fluid dynamics studies often requires separate measurements to determine physical properties of the PDMS sample relevant to the phenomena under study.
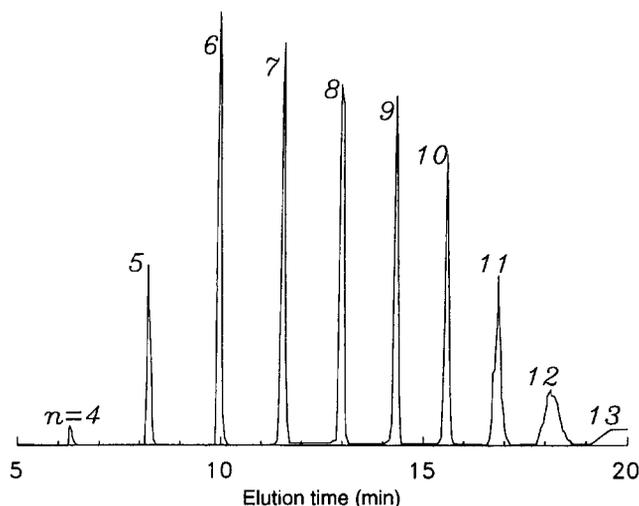
More significantly, the multicomponent nature of PDMS can adversely affect the dynamics in some fluid experiments. Consider, for example, the case of surface-tension-driven Bénard convection where a horizontal liquid layer is bounded from below by a heating plate at a temperature T_p and from above by a free interface with a gas layer (Fig. 2). In modern experiments, the gas layer is maintained to uniform depth by bounding from above with a window whose temperature is held fixed at $T_w < T_p$. For $T_p - T_w$ sufficiently large, surface tension gradients at the free surface drive hexagonal convection flows in the liquid layer. If the liquid layer is composed of a low viscosity commercial blend of PDMS, an oily film that replicates the convection pattern rapidly accumulates on the underside of the window (Fig. 3a). (The gas layer itself is not subject to buoyant instability; the Rayleigh number for the gas layer is typically < 1.) An analysis of the residue demonstrates that the lowest molecular weight components from the heated PDMS layer condense at the cooled window (compare Fig. 1 and Fig. 3b). These deposits can, in turn, spatially modulate the imposed temperature and perturb the dynamics of pattern formation. Other effects in convection experiments can arise from the multicomponent nature of commercial PDMS fluids; recent experiments suggest the presence of Soret effects (coupling between temperature and concentration gradients) with buoyancy-driven

Fig. 1. Gas chromatogram indicating the polymers with $n < 14$ in a commercial sample of PDMS (silicone oil) with a nominal kinematic viscosity of 10 cS. The number near each peak identifies the polymer length according to chemical formula given in (1). The area under each peak is roughly proportional to the relative concentration of the corresponding polymer; see text for further details of the gas chromatography analysis
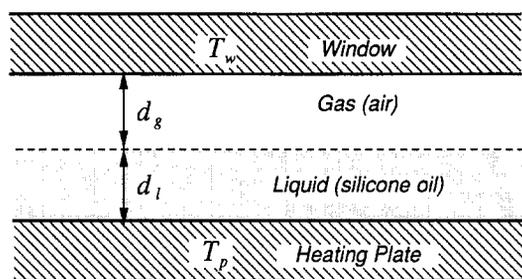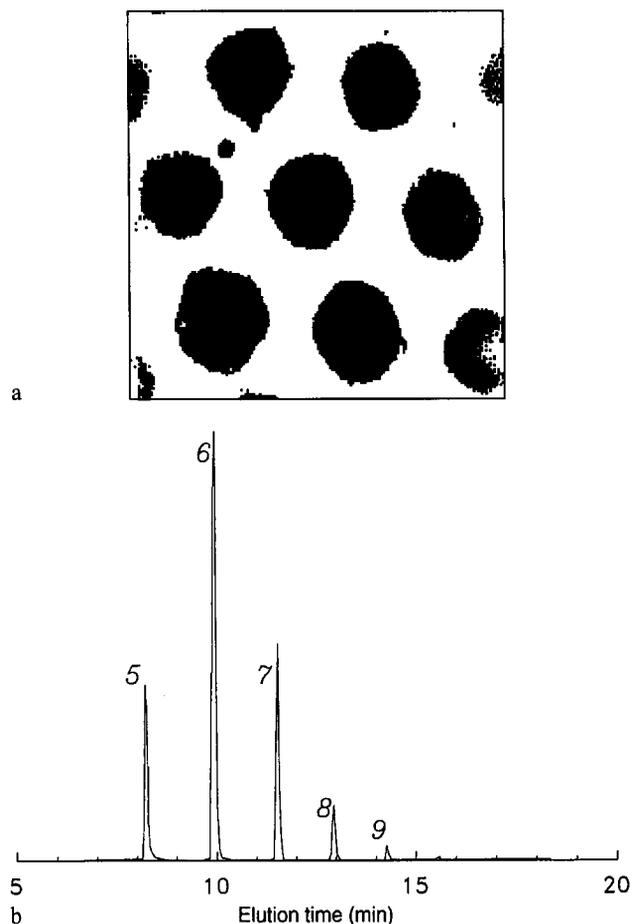

Fig. 2. Schematic of a surface-tension-driven Bénard convection experiment. Typically, the thicknesses of the liquid layer d_l and the gas layer d_g are ~ 1 mm, the heating plate temperature is $T_p \sim 25\,^\circ$C, and the imposed temperature difference $T_p - T_w$ is $\sim 10\,^\circ$C in the convection regime

Fig. 3a, b. PDMS condensation on the cooled window duplicates the hexagonal Bénard convection pattern present in the liquid layer. Such residues are observed in typical experiments (Fig. 2) when the liquid layer is a low viscosity (10 cS, in this case) commercial silicone oil. Shown here is a digitally enhanced image; when viewed under white light, the condensate exhibits multiple colors characteristic of thin film interference (a); Gas chromatography demonstrates that the condensate of Fig. 3a is composed of the lowest molecular weight polymers from the liquid layer (compare to the gas chromatogram in Fig. 1) (b)

(Rayleigh-Bénard) convection in PDMS (Moses and Steinberg 1986).

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Experimental methods and discussion

Low viscosity single-component PDMS fluids can be obtained from commercial mixtures by vacuum distillation (Wilcock 1946; Hunter et al. 1946). We employ a spinning band distillation column (Nester/Faust, Patent #2,712,520) illustrated in Fig. 4. Dual heaters provide independent control of the boiler temperature T_b and of the column temperature T_c; both temperatures are measured using thermocouples (type K). A platinum gauze spiral band of positive helicity is spun at 500 rpm (clockwise from above) to force the PDMS vapor upward and outward toward the column wall during distillation. A mechanical vacuum pump maintains the pressure inside the apparatus at approximately 100 mTorr.

Standard gas chromatography is performed on the dis tillation samples to check purity. For our analysis, we use a gas

chromatograph (Varian Model 3400) with a 13 m long, 0.32 mm ID capillary column with DB5 as the stationary phase and helium as the mobile phase; the initial temperature of the capillary column is 60 °C and is increased at a rate of 10 °C/min. The output of the chromatograph is detected using a mass spectrometer (Finnigan 700). System sensitivity is limited by the maximum temperature of the transfer line between chromatograph and the mass spectrometer. As a result, PDMS polymers with $n > 13$ cannot be detected. The chromatograph and mass spectrometer are calibrated using a purified reference sample ($n = 10$).

We illustrate the purification protocol by describing the double distillation of the $n = 10$ polymer hexacosa-methyldodecasiloxane. For the operating pressure of 100 mTorr, we compute the boiling point $T_{bp} = 152\,^\circ$C for the polymer using vapor pressures curves from the literature (Wilcock 1946). Beginning with 175 ml of commercial PDMS blend (10 cS Dow Corning® 200 fluid), we perform the first distillation by setting $T_c = 0.85\,T_{bp}$ and $T_b = 1.45\,T_{bp}$ for
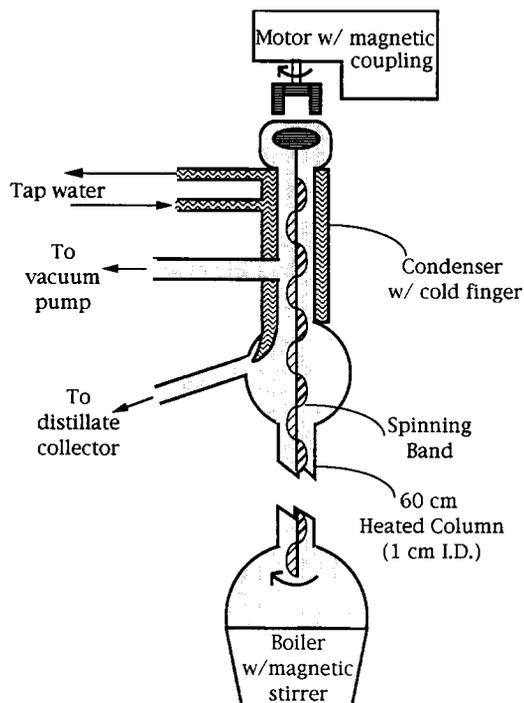
Fig. 4. Schematic of the spinning band distillation apparatus used to purify PDMS
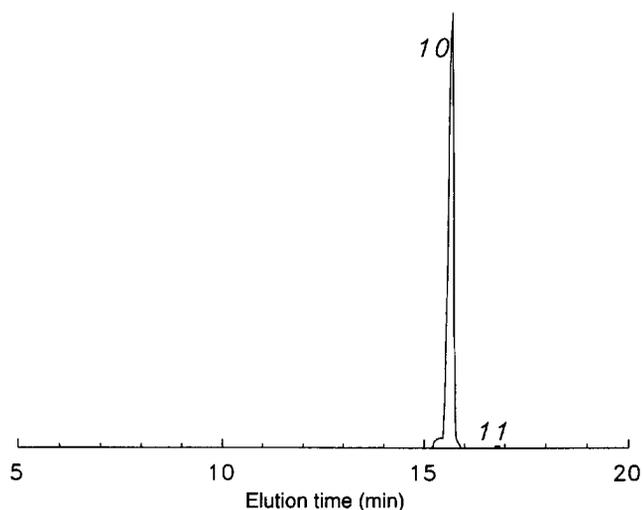

Fig. 5. Gas chromatogram of the doubly-distilled $n = 10$ polymer (hexacosamethyldodecasiloxane) fluid with an estimated purity of better than 95%

a period of about 24 h to remove most of the lighter polymers ($n < 9$). We then increase T_c to $1.03 \, T_{bp}$ and T_b to $1.68 \, T_{bp}$ and collect in a 24 hr period approximately 20 ml with a large percentage of the $n = 10$ polymer. This first distillation is repeated three times; each repetition begins with a fresh sample of commercial PDMS blend. All the once-distilled fractions are combined and returned to the boiler for a second stage of distillation. The initial temperatures $T_c = 0.7 \, T_{bp}$ and $T_b = 1.4 \, T_{bp}$ are increased slowly while maintaining $T_b - T_c = 110 \,^\circ\text{C}$. The distillate is repeatedly tested until the $n = 10$ polymer is observed to dominate in the chromatograms;

this occurs for $T_c = 0.8 \, T_{bp}$ and $T_b = 1.5 \, T_{bp}$. With the temperatures held fixed, the distillate is then collected over approximately a 24 hr period.

Figure 5 illustrates the purity of the $n = 10$ after double distillation in the spinning band apparatus. We estimate the purity of our sample (approximately 3 ml) to be comparable to a 97% pure reference sample obtained from the Dow Corning Corp.; the dominant impurity in our sample is the $n = 11$ polymer, whose peak can barely be seen in Fig. 5. This purified fluid yields no condensation in our surface-tension-driven Bénard convection experiments because the vapor pressure of the $n = 10$ polymer (7 cS kinematic viscosity) is 6×10^{-7} Torr at $25 \,^\circ\text{C}$, as compared to 4×10^{-3} Torr at $25 \,^\circ\text{C}$ for the $n = 5$ polymer present in commercial 10 cS PDMS fluid (Figs. 1 and 3a). In addition to the sample just described, we obtain approximately 10 ml of $n = 10$ polymer with greater than 90% purity; similar quantities of the $n = 9$ polymer are also obtained with comparable levels of purity.

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Conclusions

This simple protocol yields single-component PDMS with well-defined physical properties. Both the separation and the analysis techniques are commonplace in many research laboratories. With small improvements to the analysis methods we used, our approach should yield high purity separation of PDMS for $n < 15$ (kinematic viscosity less than 15 cS); purification for higher n becomes more difficult as the temperature difference between boiling points decreases with increasing n. In cases where higher purity is desired, additional separation may be possible using preparative chromatography techniques. A similar protocol should enable separation of single-component species in other polymeric liquids used in fluid experiments (e.g., the perfluorinated Fluorinert™ liquids manufactured by the 3M Corporation).

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