

BUTYL ACETATE, AN ALTERNATIVE DRILLING FLUID FOR DEEP ICE CORING PROJECTS

By

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ABSTRACT. Deep drilling operations in glaciers require a fluid at and below the brittle zone. Many past practices have employed various formulations using fuel oil as the base. The case for butyl acetate is presented here as a dense, and environmentally-safe drilling fluid.

INTRODUCTION

Most deep ice coring projects of various nations have, because of cost and logistical reasons, used a variety of fuel oil-based drilling fluids. In virtually all cases a densifier such as PER (perchloroethylene) or TCE (trichloroethylene) have had to be added to bring the fluid density up to that of ice in order to prevent the collapse of the deepest parts of the hole. We are aware of two variations from this practice: one of the use of alcohol, about which we will briefly comment later, and two, a field test of an oil-well drilling fluid known by the tradenames "permoil," or "bromoil," a dilute solution of PBBE (poly-brominated biphenyl ether) in a more refined hydrocarbon known as LVT-200. It should be noted that bromoil was developed for high temperature well boring, and not low temperature ice coring. LVT-200 appears, by gas chromatography-mass spectrometry, to

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be a mixture of saturated branch chain and saturated cyclic compounds. However, all hydrocarbons are not dense enough, and their viscosity far too high to permit timely operation at deep (≥ 1000 m) drill sites. Furthermore, any planned use of PBBE as the densifier is less acceptable than the use PER or TCE, all of which are hazardous to health and environment. The chemical structures of butyl acetate, anisole and several other compounds mentioned in this article are shown in Figure 1.

The use of PER and TCE poses significant health safety and environmental risks. Both PER and TCE have known and suspected carcinogenic properties (PICO TR 89-2 and references therein), and add to the already undesirable load of atmospheric organic chlorides. It should also be noted that PBBE is a viscous semi-solid material (Brackenridge and McKinzie, 1988), and is on the United States Environmental Protection Agency's (EPA) list of "Extremely Hazardous Substances" and falls under the EPA's "Community Right to Know" (Sax and Lewis, 1989). Moreover, the brominated components are resistant to biodegradation as are DDT, PCB (polychlorinated biphenyl) and PBB (polybrominated biphenyls), all of which have been shown to concentrate in the food chain, and to have deleterious long-term effects on the health of individuals who have been exposed to relatively low levels (e.g., Watanabe *et al.*, 1987; Mulligan *et al.*, 1980; Sundström and Hutziner, 1976) and are potent inducers of xenobiotic metabolism (Carlson, 1980 a, b).

The Polar Ice Coring Office (PICO) conducted a chemical literature survey in an effort to identify a drilling fluid suitable for deep ice coring that would have the appropriate viscosity and density characteristics, a fluid that would minimize potential health and safety risks for workers, and cause minimal environmental impact. The results were published in two technical reports (Gosink, 1989; Gosink *et al.*, 1989). This article briefly reviews these reports, and presents a case for the use of butyl acetate as a deep ice coring drilling fluid.

Of nearly 250,000 compounds electronically surveyed, 11 potential drilling fluids tentatively were identified as suitable. Of these 11, only two, butyl acetate and anisole, fully meet the constraints imposed by technical, scientific, health, safety and concerns mentioned earlier. This report discusses the chemical and physical characteristics of butyl acetate and anisole with respect to their use as a drilling fluid, and presents some important technical considerations with respect to health, safety and the environment surrounding the use of these compounds. Butyl acetate alone at lower temperatures (-20 to -78°C) meets and exceeds the desired physical characteristics of density and viscosity. The cost of butyl acetate is reasonable (\$0.43/lb [\$0.95/kg]). Both butyl acetate and anisole (>\$2.00/kg) are totally synthetic, i.e., derived from petroleum products, thus presenting no carbon-14 complications. Recommendation of butyl acetate is also based on the facts that even-numbered carbon chains (e.g., butyl- 4) are less toxic (narcotic) than the odd numbered (e.g., propyl- 3 or amyl- 5), and it is more readily available.

DISCUSSION

Density

The hydrostatic pressure, which is a function of density and depth, is of major importance in the selection of ice core drilling fluids. The density of butyl acetate rapidly increases with decreasing temperature (Figure 2) and at temperatures below -15°C is sufficient, being greater than the firn-ice-layer density of 0.90 (Patterson, 1981). At -30°C the density of butyl acetate (Figure 2) is more dense than pure ice (Ashton, 1986). A 10% mixture of anisole in butyl acetate is as dense as pure ice at -15°C. Typically, in other deep cores, the top of the fluid level is about 100 m below the ice surface to balance the ice matrix pressure. Since the average internal temperature in the Greenland glaciers has been observed to be -31°C, and is expected to be significantly colder in Antarctica, an added densifier is not required. If a

densifier is required for more temperate glacier drilling operations, anisole is much more desirable than PCE, TCE or PBBE with respect to water pollution, human toxicity and air pollution.

Viscosity

The viscosity of the fluid is important to the travel time of the drill string, particularly at greater depths, and thus to the overall cost of the project. Either a low viscosity fluid must be employed, or alternatively, larger-diameter (more expenditure of time and energy) holes must be bored to accommodate the high viscosity fluids such as bromoil. Figure 3a shows the effect of drill fluid viscosity on velocity of the fall of the 1250-lb drill string to be employed in the 1990 Greenland Ice Sheet Project. At 10 cp it is about 4 sec/m; at 2 cp about 1 sec/m, thus butyl acetate will cut this major portion of the operation time by a factor of four compared to bromoil with a viscosity of ca. 15 cp at the observed average internal glacier temperature of -31°C. Figure 3b shows the round trip time for the drill string going to 1000 m depth. It is calculated to be about 10 min with butyl acetate, but nearly an hour and a half with bromoil with its viscosity of about 15 cp at -30°C. Depths of 3000 m are anticipated.

The general desire is that the viscosity of the drill fluid be less than 5 cs (nearly 5 cp; $cp = cs \times \text{den.}$). As can be seen in Figure 4, the viscosity of butyl acetate (and the 10% anisole mixture) remains well below 3 cp, even at -50°C, whereas the viscosity of 0.91 bromoil is substantially above 15 cp at anticipated ice temperatures. With the exception of the three points labeled "Lit." all of the data in Figure 4 were determined in this laboratory using a falling ball type viscometer. The viscosity estimated by the manufacturer of LVT-200 at -40°C is also indicated in Figure 4 as "Lit", and fits well with our experimental data and is comparable to other fuel-oil mixtures. It can also be seen that the addition of a small quantity of PBBE to LVT-200 in the formulation of bromoil raises the viscosity even higher.

Volatility/Flammability

The greater volatility of butyl acetate raises fire safety questions, but it is unlikely that under the conditions experienced in ice-core work that this will be a problem. There is confusion in the technical literature on the flash point of butyl acetate. Sax and Lewis (1989) report 72°F (22°C); 92°F (33°F) on a bottle of high quality butyl acetate, suggesting a common error of "7" for a "9," and the Merck Index (1976) quotes 38°C (100°F). Determination of the flash point by a local independent testing laboratory indicated 85°F (29.4°C), in keeping with our observations. In Figure 5, the handbook vapor pressure of s-butyl acetate is plotted against temperature. The curve for n-butyl acetate is reasonably estimated from the fact that the boiling point of the n-butyl isomer is 2% higher, on the absolute temperature scale, than that of the s-butyl isomer. Published safety data states that the lower flame limit concentration of n-butyl acetate in air is 1.7%. This corresponds to a vapor pressure of 12.9 mm Hg, achievable only in an unventilated closed room or container at 24°C. At -20°C (-4°F), an average to cool day on the drill site, the maximum possible air concentration of butyl acetate in an unventilated area would be approximately 1300 ppm (0.13%), well below the lowest published (1988-89 CRC handbook) lower flame limit of 1.4% (Figure 5). Figure 5 further indicates that at the higher altitudes where drilling operations will occur, the lower flame limit is still in the +15°C to 18°C range.¹ The warmest part of the drill site days, according to temperature records from past sites, rises to be about 0°C. Odor detection and irritation both occur below the permissible exposure limit (150 ppm), and thus provide both adequate physiological and fire-warning properties.

Theory was tested by applying a lit paper match to a small beaker of butyl acetate at laboratory temperature (ca 24°C). The butyl acetate ignited only by briefly

¹ Calculated for an air pressure at an average of 2300 m altitude (7000 ft) of 575 mm Hg.

touching the flame to the surface, but it went out as the match was immediately withdrawn. The experiment was repeated twice more outside where the temperature was approximately 4°C. The butyl acetate would not ignite, and in fact, extinguished the match. There was a slight flare as the glowing match head touched the surface, but all of the flame was extinguished as the match was plunged below the cold liquid surface.

Side benefits of the greater volatility of butyl acetate are:

- 1) No oily residue will remain on work-clothes between shifts of drilling crews.
- 2) Residual odor will disappear rapidly depending on degree of ventilation.
- 3) The core will be much less "greasy" to handle.
- 4) The lower viscosity and higher volatility should pose less of a hazard for making the driller's deck slippery.

Solubility

Several experiments were performed in which a 20-g cube of ice was placed in a covered beaker with about 100 mL of solvent as shown in Figure 6. The published solubility of butyl acetate in water is about an order of magnitude lower than ethyl acetate, and is essentially the same as that for PER, about 0.7%. The solubility of water in butyl acetate is 1.6%. Note that the weight loss of ice in wet butyl acetate was not noticeable in seven hours contact time. It has been reported that Soviet drillers have utilized alcohol as the drilling fluid at their sites. However, our experiments show that pure alcohol causes a rapid solution of the ice (Figure 6). No attempt was made to study 50% ethanol-water mixtures because even if there were not appreciable weight loss, it is anticipated that the water exchange would be unacceptable for oxygen isotope studies.

Solvent Effect on Polymers

The effect of butyl acetate and several other solvents on a variety of polymers is shown in Table 1. Both butyl acetate and anisole have no effect on the various polymeric materials employed in the PICO deep drill string. Recent inquiry about various epoxy resins and other plastics also show no deleterious effects. The wires in the electric motor, even at temperatures of 125°C, were not affected by either butyl acetate or the 10% mixture of anisole. The drill motor, which contains brushes, has recently been operated successfully at full power immersed in butyl acetate at ca. 25°C for over 700 hours. Furthermore, the manufacturer stated that the tensile strength of the Kevlar cable used in PICO's drilling operations is not affected by butyl acetate. (Letter from Cortland Co., Oct., 1989).

Trace Elements

A recent analysis of a grade ($\geq 99.5\%$) of butyl acetate indicated contaminant concentrations of: $<0.01\%$ water, 0.07% butanol and $<0.01\%$ acetic acid. An analysis based on a 1:1 water extraction was reported as: chloride, <0.5 ppm; sulfate <0.1 ppm, i.e. below the routine detection limits of the analyzer, and therefore of no threat to trace element analyses of ice cores even if 1% of butyl acetate is trapped in the outer portions of the core. No data are available on the residual trace inorganic pollutants in fluids such as fuel oil, LVT-200 or PBBE, etc.

Indoor Ambient Air Quality

Butyl acetate odors are detectable at 10 ppm. At approximately 100 ppm ambient concentration, some nasal irritation may be noticed. This is well below the Occupational Health and Safety Administration's (OSHA) limit of 150 (710 mg/m^3). Kerosene fumes, it should be noted, are only permitted to be 100 mg/m^3 of air. Anisole odors are detectable at 0.2 ppm, but no OSHA standards have been set. Therefore, before any significant health hazard would be present, odors would be noticeable and

irritating. Given that anisole, if used, will be used in such low amounts, no special precautions will be necessary above those which should be instituted for butyl acetate.

Potential problems of excessive butyl acetate concentrations in the air can be eliminated by proper design and use of ventilation systems in the drill enclosure, core relaxation pit and science trench. Fans to keep the interior core handling structures cold should be part of any management plan, and will thus automatically insure that butyl acetate vapors will be kept to an acceptable minimum.

Health Hazards

Butyl acetate is slightly hazardous to health. It is a mammalian reproductive toxin. The main risk, however, comes from prolonged inhaling vapors in excessive concentrations. Anisole has no specific health hazards and is not a mammalian reproductive toxin. Neither butyl acetate nor anisole is listed as a carcinogen as are PBBE and TCE. Several inexpensive battery- or a.c.-operated alarms are available on the market at a cost of \$300 to \$1200 each. These alarms are sensitive enough to warn at the parts per million level for health purposes, or at higher ranges for fire danger warning, and operate at -5°C without the need of a warmed housing.

Environmental Characteristics

From an environmental aspect, butyl acetate (and anisole) is a single, easily biodegradable compound as opposed to the mixture of components in fuel oil, LVT-200 or PBBE. Both fuel oils and LVT-200 pose higher environmental risks since, in the event of a spill (or the long-term eventual release of residual material left in the glacier), they have a long residence time, particularly in a cold environment (Figure 6). In a worst case scenario, if all the butyl acetate leaked out the bottom and flowed into a fjord, most of it should evaporate in one to three days. An additional

small amount would disperse in the water column, where it would be rapidly biodegraded. Butyl acetate will, contrary to all the other fluids proposed or in use, totally clean itself up in a matter of days, even in a cold climate. Anisole would behave similarly. LVT-200, and other hydrocarbon solvents on the other hand, is not readily biodegradable, and would not evaporate appreciably. Thus, virtually all of the hydrocarbons would have to be physically removed from the water surface, particularly in view of the toxic densifier materials, whether it be PBBE or TCE, etc.

Anisole is not as biodegradable as butyl acetate, but should not have a high environmental residence time. If the use of a densifier is required in temperate glaciers (average internal temperature $\geq -20^{\circ}\text{C}$), anisole should be acceptable in comparison to other commonly used densifiers from an environmental standpoint.

SUMMARY AND CONCLUSIONS

Butyl acetate represents a significantly lower risk to the environment and to the worker than bromoil, LVT-200, or fuel oil with PCE. Both fuel oil and LVT-200 are resistant to environmental degradation and subsequently have long residence times in the environment. Persistence of these hydrocarbon compounds and their densifier components is increased in cold temperatures. In the event of a spill, or in the inevitable long-term release of residual material left in the glacier, the persistence of these compounds will represent a grave environmental hazard. In contrast, butyl acetate is relatively easily degraded in the environment. Furthermore, any unexpected releases or spills should evaporate quickly and present little environmental or safety hazard.

The fire hazard of butyl acetate is very low at temperatures below about 0 to 10°C and thus does not pose any inordinate danger.

Contamination of the ice core by butyl acetate or trace containment appears to be acceptably low for most chemical and physical measurements.

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Table 1. SOLVENT EFFECT ON POLYMERS (24±3 hrs).

Plastic	No. 1 Fuel Oil	0.91 Bromoil	PER	LVT-200	Anisole	n-Butyl Acetate
Black Rubber	ss-	ss+	ss+	ss+	se	se
Polypropylene	ss-	ss	ne	se	ne	ne-
Teflon	ne	ne	ne	ne	ne	ne
Viton	ne	ne	ne	ne	ne	ne
Elec. Insul.*		ne	ne		ne	ne
Elec. Insul.†						ne
Polyethylene						ne
Kevlar						ne
Nylon						ne

se = slight effect

ss = soften and/or swell

+ = more;

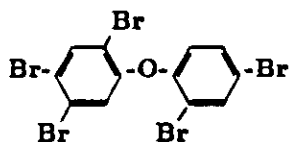
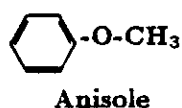
- = less--i.e., a very slight effect or softening

ne = no effect (did not swell, soften or become tacky)

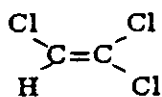
* Lacquer on wire, 125°C for 2 hrs.

† Plastic jacket on wire.

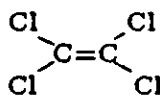
A blank area indicates no data.



PBBE
(one of several isomers)



TCE



PCE

Figure 1. Chemical structures for butyl acetate, anisole PBBE, TCE and PCE.

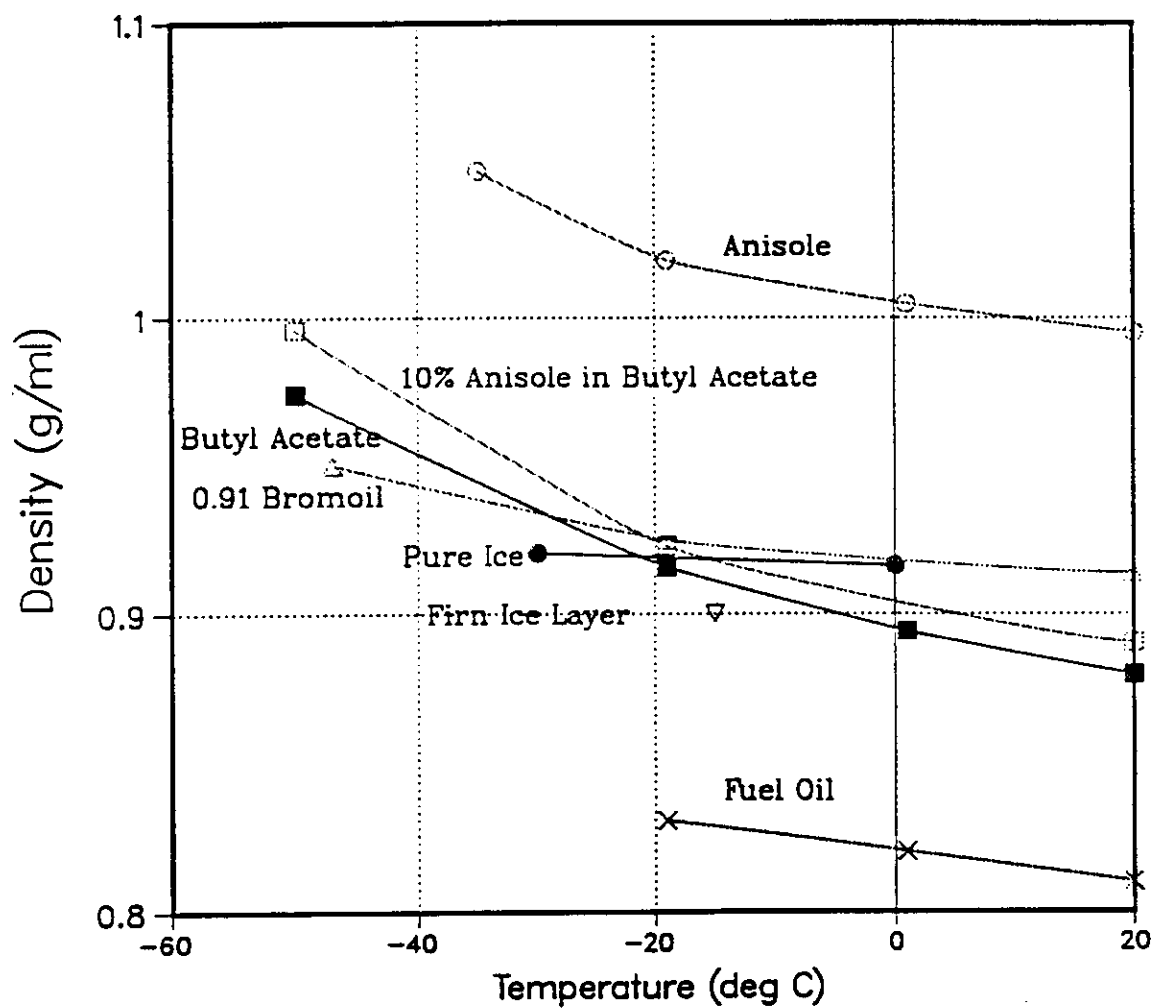


Figure 2. Density (g/mL) of potential ice drilling fluids versus temperature (°C). Fuel oil (×); pure ice (●); 0.91 bromoil (Δ); butyl acetate (■); 10% anisole in butyl acetate (□); anisole (o).

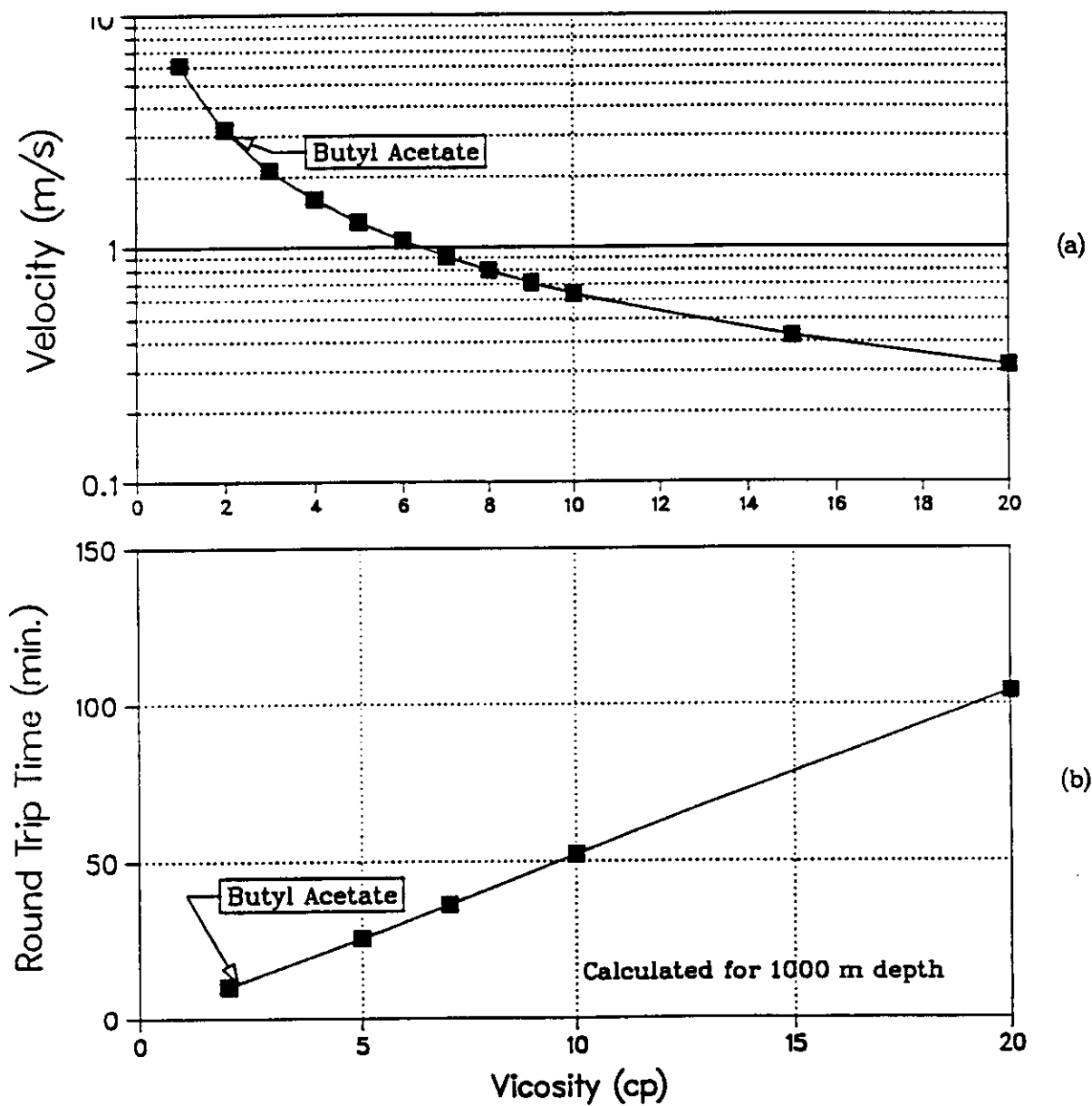


Figure 3. (a) Drill string fall velocity as a function of the drill fluid viscosity. (b) Drill string round trip travel time as a function of drill fluid viscosity.

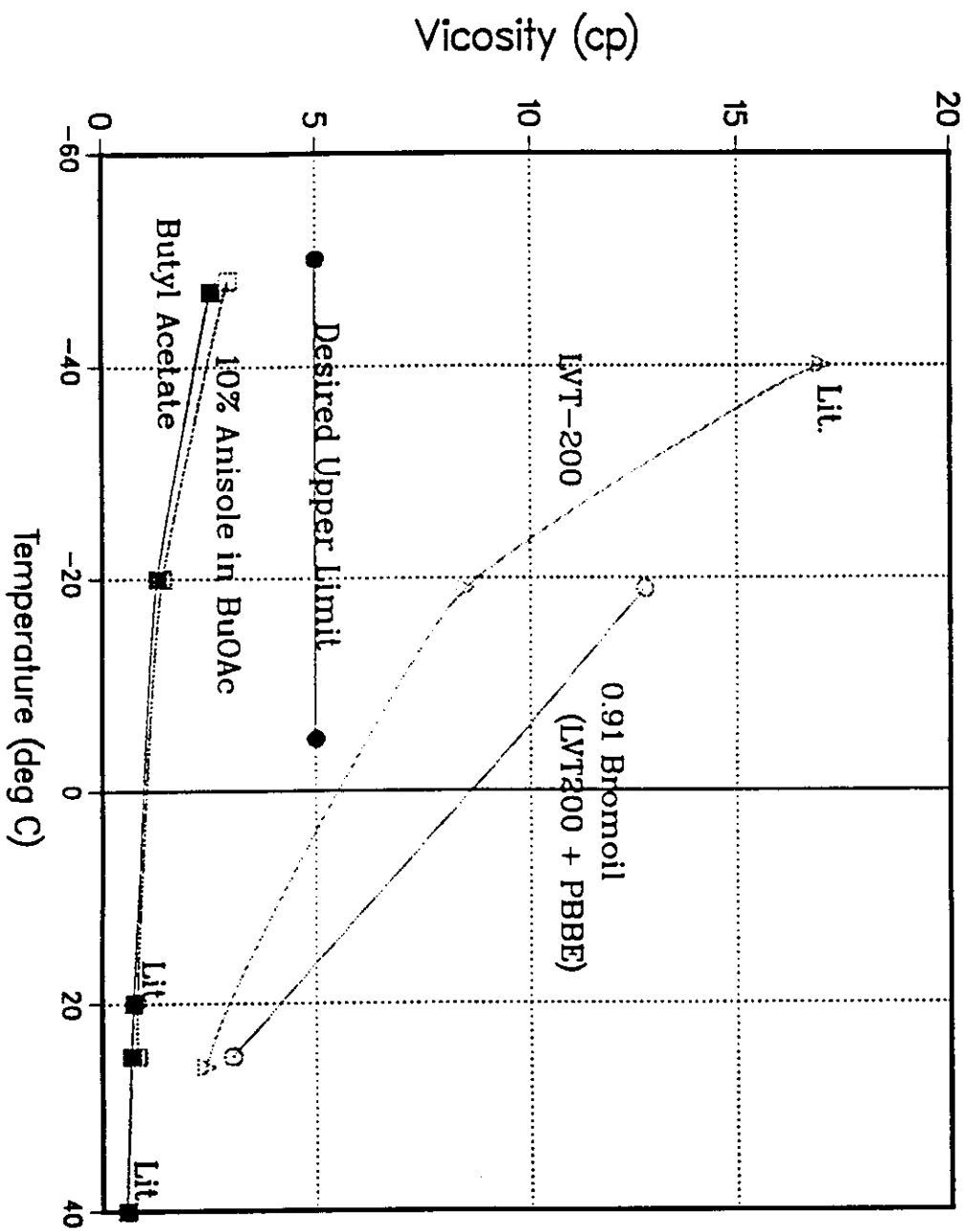


Figure 4. Viscosity (cp) of potential ice drilling fluids versus temperature (°C). Butyl acetate (■); 0.91 bromoil (○); 10% anisole in butyl acetate (□); LVT-200 (Δ). "Lit." = literature data points.

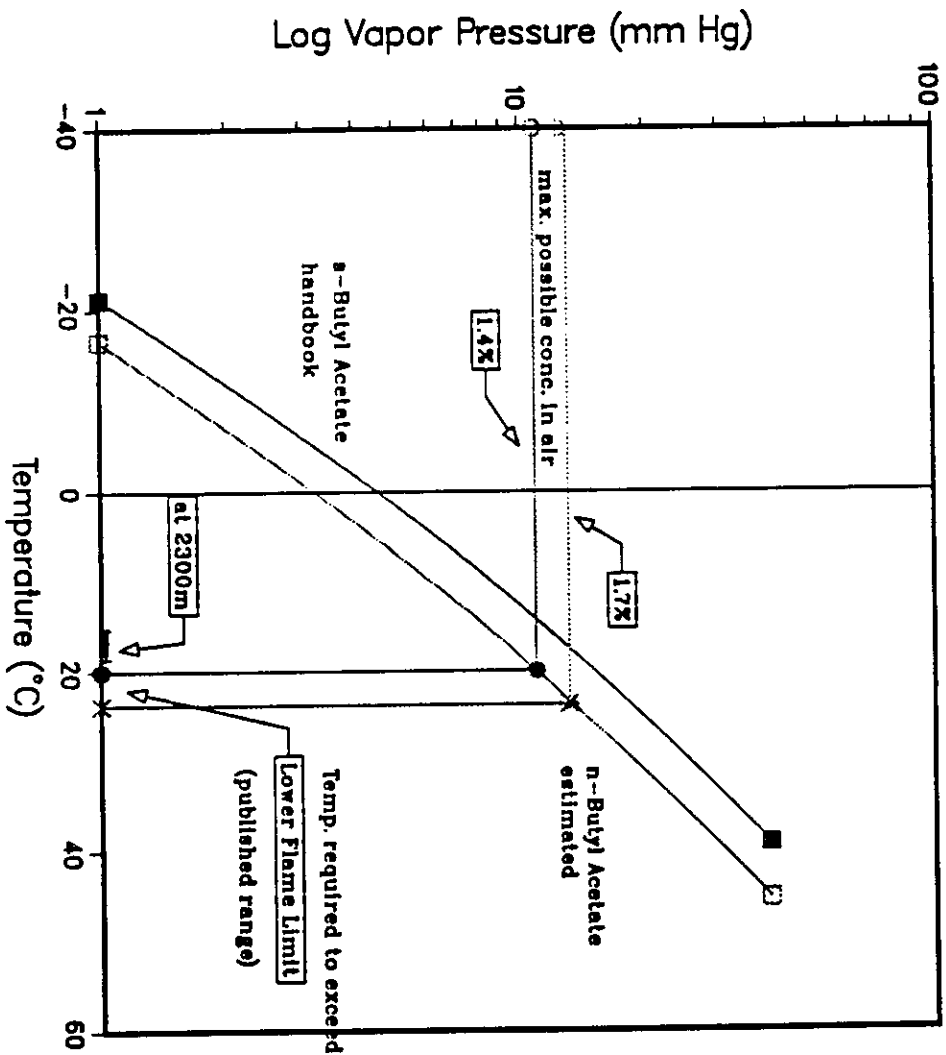


Figure 5. Vapor pressure versus temperature of butyl acetate, indicating the temperature required to exceed the lower flame pressure/concentration at sea level and at 2300 m (7000 ft) altitudes.

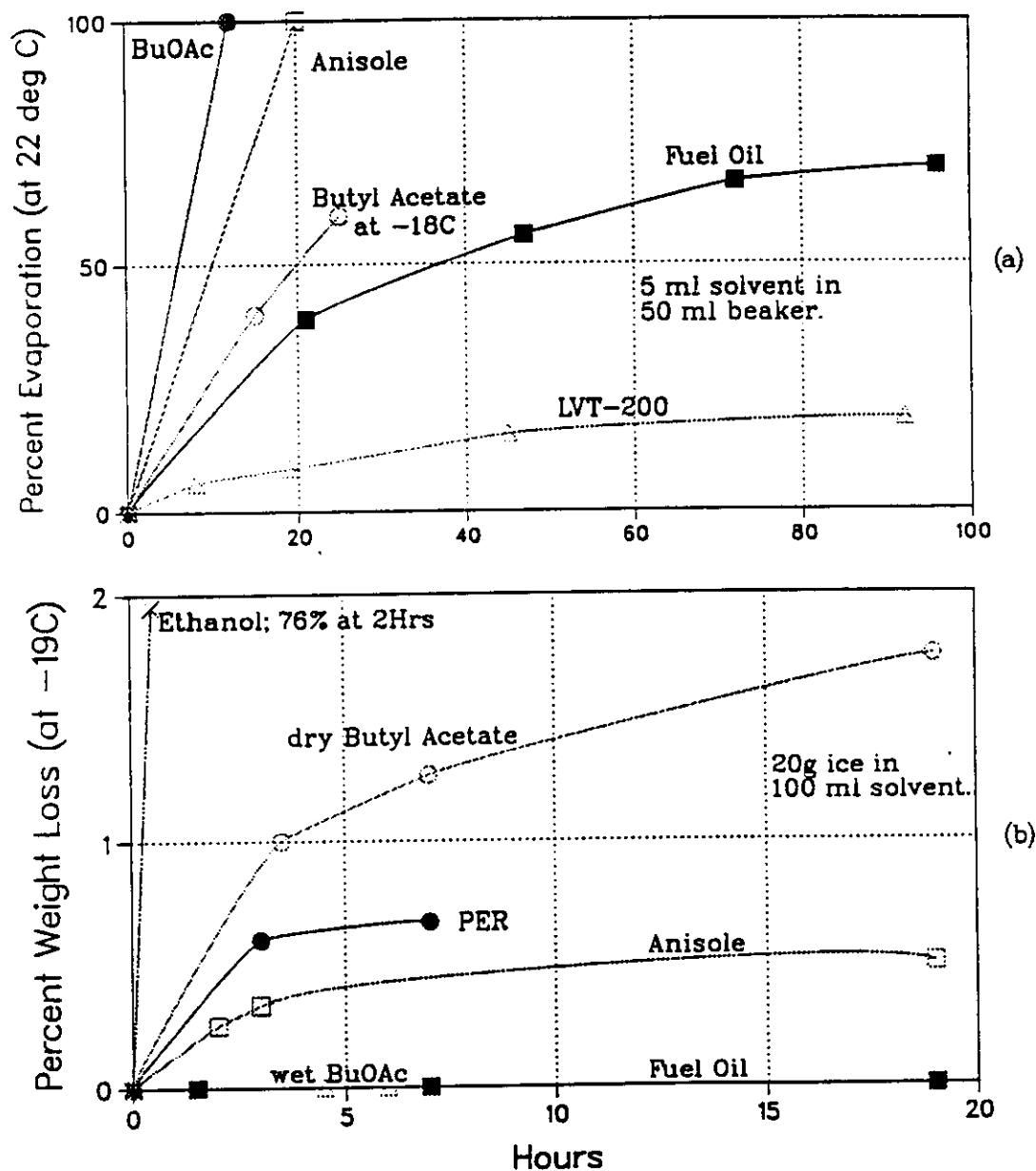


Figure 6. (a) Percent evaporation of drilling fluids (at 22°C) versus time (5 mL of solvent in a 50 mL beaker; (b) Percent weight loss of ice in potential ice drilling fluids at -19°C (approximately 20 g of ice in ca. 100 mL of solvent)