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AQUEOUS ETHANOL AS AN ICE DRILLING FLUID

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ABSTRACT

Aqueous ethyl alcohol (and ethylene glycol) solutions have a substantial history of use in a variety of deep ice drilling projects. This report considers such factors as ice corrosion, penetration, density, viscosity and safety of aqueous ethanol (and of ethylene glycol) as an ice core drilling fluid. The cost and environmental factors for ethanol as a drilling fluid are very good, but aspects such as viscosity and ice corrosion are not.

INTRODUCTION

Ethylene glycol solutions have been employed for several decades in deep ice drilling projects (e.g., Ueda and Garfield, 1969a) and aqueous ethanol for a decade or more (e.g., Zagorodnov, 1982; Morev *et al.*, 1982). Fuel oils containing small quantities of halogenated compounds to increase the density of the mixture have also been employed in deep ice drilling projects for several decades (e.g., Ueda and Garfield, 1969b). We have advocated and employed butyl acetate as the drilling fluid in Greenland (Gosink *et al.*, 1991). There are several desirable features for the use of aqueous ethanol as an ice drilling fluid (cost, environmental and personal safety) but there are serious questions about its viscosity and density that the user must also consider, not to mention its propensity to corrode the ice. Alcohol, and particularly glycol solutions become extremely viscous at low temperatures (e.g., Hansen, 1976;

Ueda and Garfield, 1969a; op. cit.) and present some density overturn problems if the bottom of the bore hole is significantly warmer than the upper reaches of the hole. Aqueous ethanol is an improvement over ethylene glycol with respect to density and viscosity problems, is decidedly cheaper to employ than even fuel oils, and is safe for both the workers and the environment. However, the potential for corrosion of the ice sample is greatest with alcohol, even at low temperatures.

We have examined the available literature and conducted laboratory and field tests to ascertain whether or not aqueous ethanol could be used as a reliable drilling fluid for retrieval of glacier ice cores for chemical and physical analyses.

DISCUSSION

Corrosion

Aqueous alcohol can rapidly attack ice. It attacks the ice when either temperature or concentration equilibrium conditions are not met. An aqueous ethanol solution just a few per cent rich in alcohol concentration for the given temperature conditions, or an alcohol solution warmer than equilibrium conditions, will rapidly attack ice. A simple test was performed on approximately 20 g cubes of ice placed in beakers containing 90 ml of aqueous ethanol (32% alcohol), all in a freezer at -22°C. The solvent in these tests effectively overwhelms the ice compared to the reverse situation in an ice coring hole. However, this experiment rapidly demonstrates the corrosive effect of aqueous ethanol on ice. The control case consisted of ice in aqueous ethanol at equilibrium conditions. The results are shown in Figure 1. The 1.2% loss in the control is ascribed to the repeated brief handling in a warm room during the weighing operations. The "rich" case was aqueous ethanol at -22°C, but containing a slight excess (less than 4%) of alcohol. One can see that even after 4 h, equilibrium has not been achieved. Equilibrium would be achieved after a 21% loss of weight by the ice. In the "warm" case, the aqueous ethanol was warmed to -10°C before the -22°C ice was introduced, all in the freezer. After 20 min the aqueous alcohol temperature was -14°C, and had rapidly attacked the ice during that period. One can also see (Fig. 1) that the ice weight loss in this "warm" case stabilized after two hours. Both of these examples show reasonably anticipated problems in deep ice drilling operations, ones which will lead to either partial destruction of the all important core sample, or inordinate production of slush which can jam the hole. Humphrey and Echelmeyer (1990) refer to the latter problem as the antifreeze paradox. Since the internal temperature of the bore hole varies with depth (generally colder at the top), the ratio of water to alcohol must constantly be monitored and changed. Addition of heat will keep the hole open (e.g., Ueda and Garfield, 1969a), but is potentially destructive of the core for sensitive chemical measurements, and unless heat is maintained throughout the operation, severe slush formation or refreezing will occur (Humphrey and Echelmeyer, 1990).

In a separate corrosion test in the field, ice cores from 130-m depth at Summit, Greenland were immersed in red dyed aqueous ethanol (26%) at equilibrium conditions (ca. -15°C) for 15 minutes, and for over two hours. (The few tenths of a percent of water soluble dye was obtained from Cole-Parmer, part number N-00298-05.) Both core samples were intensely pink in color when removed from the deeply dyed aqueous ethanol bath, but became colorless to the unaided eye when they were rinsed with more of the undyed solvent, also at equilibrium conditions. After 15 minutes contact, tool marks (*ca.* 0.5 mm deep) were still visible, but fracture marks on the top of the ice were rounded. No pitting was noted on the side of the short term exposure core. The core exposed over 2 h to equilibrium aqueous ethanol shows significant rounding of the tool marks and slight pitting. In addition, slight, irregularly spaced penetration of the dye was observed. The dyed spots appear to be less than 2 mm in depth and length.

Penetration

Figure 2 shows the penetration of aqueous ethanol in samples of Greenland ice. Trace "a" is from the sample treated with dyed alcohol (26%) at -15°C for 15 minutes in a cold room at Summit (GISP-2), Greenland. In yet another penetration experiment (trace b), aqueous alcohol (50% by volume) was introduced to the then ca. 150 m (-31°C) depth secondary bore hole at Summit, Greenland, at the end of the drilling season. The depth of the fluid was about 15 to 20 m. A short core was drilled and returned to this laboratory for analysis. About three months later, the cold-stored cores were lathed and the melted shavings analyzed. (Other samples taken at an earlier date were scraped from all of the test cores described above, and showed essentially the same results as those shown in Fig. 2.) Analysis of the ethanol in the melted ice scrapings and turning was by flame ionization detection gas chromatography. The subsamples from the outer half- millimeter surface of the dye exposed ice were the only ones to exhibit a slight pink color. Samples from deeper in the ice were colorless. Chemical analysis revealed that most of the alcohol (≥10,000 ppm) remained in the outer 1 to 2 mm of the core, but that chemically significant penetration occurred to 15- to 20-mm depth (and by implication, a factor of four or more of foreign water). Alcohol was not detected in any of the samples from the entire center 60-mm diameter portions of all the ice core samples. Replicate analyses show error to be about ±3% at the 10 ppm level; ±20 % at and below the 1 ppm level. The detection limit for the method is ca. 0.2 ppm. The level, or stair step, in the penetration curves is real, having been observed in several separate samples and separate scraping or lathing experiments. Penetration by hydrophobic butyl acetate is also shown in Figure 2 (trace c). The concentration of the entrained butyl acetate is one to two orders of magnitude lower than the results for alcohol. Trace metals (copper, chromium) in butyl acetate from a test on a drill string were on the order of 1 or 2 ppm and with iron (probably from the container) at about 20 ppm.

The presence of 1 ppm of drill fluid would thus contaminate the ice at the part per trillion level. Aqueous alcohol will probably carry one or two orders of magnitude more trace metal contaminants than butyl acetate.

Analysis of a 1-kg block of distilled water ice, treated with aqueous ethanol at -22°C, however, showed alcohol penetration to the center at the 7-ppm level. The block was permitted to melt in a beaker in three stages. No great care for thermal stress was given to the sample. The outer and intermediate stages contained 35 and 17 ppm ethanol, respectively. The remaining ice and beaker were rinsed with distilled water between melt stages. The mechanism for the penetration is unknown, but probably through micro-fractures.

Density

Figure 3 presents density for aqueous ethanol solutions at or very near their freezing points. CRC handbook data for the density of aqueous alcohol at 20°C is provided for comparison purposes. The straight line labeled "pure ice" is an extrapolation of the 0° to -30°C density data by Paterson (1981). At -51°C the density of 72% alcohol in water appears to be slightly less than that of ice. Internal glacier temperatures near -50°C are anticipated for drilling projects in Antarctica, at least in the upper portions of the glacier, particularly in the east Antarctic plateau. Elsewhere in Antarctica internal temperatures may vary from approximately -20°C to -35°C. The required less dense fluid (72% alcohol in water) would be stable on top of the more dense solutions that would be introduced to the deeper portions of the bore hole. However, potential problems arise. One problem is that the low alcohol content, high density fluid to be pumped to lower levels in the hole may freeze in the tube passing down through the much colder upper levels. Another problem is that if heat is added to prevent freezing, then corrosion of the ice wall in the upper portion will occur, followed by slush formation when it re-cools. There are some ideas on how to circumvent these problems, but will require a commitment to operate such a drill. Adding 5% ethylene glycol to 70% ethanol raises the density to 0.93, but it also increases the viscosity to 65 cp (10% glycol, 60% alcohol = 123 cp). Viscosity is discussed in the next section.

Aqueous ethanol density is greater than those of either butyl acetate or hydrocarbon mixtures so that shavings from the coring operation may rise more rapidly, thus increasing the likelihood of slush jamming the upper portion of the hole. We have been informed (V. Zagorodnov, personal communication, 1991) that Russian drilling operations in Antarctica with aqueous ethanol have been quite successful (ca. 700 m in seven weeks) and that the holes are easily reopened in following years even though they are slush filled.

Viscosity

The viscosity data presented in Figure 4 is for aqueous ethanol solutions at or very near their freezing points. The percent alcohol content is indicated by the numbers at the top of the figure. It is desirable that the viscosity of ice core drilling fluids be 5 cp or less. A discussion of this time and energy point is presented in Gosink *et al.* (1991). In brief, it will take the drill string 10 minutes for one round trip in a 1000-m hole where the viscosity or the drill fluid is ca. 3 cp compared to 80 or 90 minutes if the viscosity is 15 cp. Fluids with viscosity of no more than 20-25 cp are workable in moderate depth holes ($\leq$1000 m). While the prospect of 50 cp fluid in Antarctic operations is not desirable, it can be overcome, and is substantially better than the extremely adverse viscosity problems associated with ethylene glycol solution. For example, Hansen (1976) used terms such as "pasty" or "difficult to work" for 20 to 50 % ethylene glycol-water mixtures. The low viscosity ($<$5 cp) is a serious problem for ball bearing lubrication, but not for roller or needle bearings. A viscosity closer to 20 or 25 cp is desirable if sealed bearing chambers must be avoided.

Safety – Personal, Environmental and Fire

Ethanol is the best of all fluids, even over our previously recommended butyl acetate, from an environmental and personal safety consideration. In the work place air, 1000 ppm of the alcohol vapors are permitted. (10,000 ppm for several hours will induce intoxication in some people and is near the fire limit.)

As far as the environment is concerned, ethanol is a natural, widely occurring product. Ethanol would be rapidly consumed by the microbiota in any water body into which it might be spilled, and its infinite solubility would assure its rapid dispersion.

The volatility of ethanol is good in terms of a land spill, but leads to some concern with respect to fire hazard. Its flash point is lower than that of butyl acetate, which is considered safe only in view of the low temperatures at which it will be utilized. The same is still marginally true for cold aqueous ethanol. Table 1 shows the flash point of ethanol and aqueous ethanol. The data were determined in a commercial testing laboratory or taken from the literature. Butyl acetate and fuel oil data are added for comparison. One mitigating factor is that only 20-70% solutions of ethanol will be employed, but the flame point for 50% or greater concentrations is at or below the temperature of the warming hut, and certainly below that of the heater element in the warm-up hut. It should be noted that alcohol has been used safely as a drilling fluid for many years by the Soviets.

Cost

By using ethanol, the potential cost saving amounts to many tens of thousands of dollars per bore hole. The manufacture cost of ethanol is about half that of butyl acetate but the major cost advantage comes not from the purchase, but in the transportation cost to the remote drill sites (about $3-4 per kg). Nominally, 50% solutions would be required and the snow will not require any (or very little) added heat because of the corrosive nature of ethanol towards snow to be used to dilute the alcohol.

Miscellaneous

The ethanol available from commercial manufacture (Quantex Corporation) is totally synthetic, derived from petroleum, thus eliminating any C-14 problems. While pure water (glacier ice) and alcohol are not good electrical conductors in themselves, one will have to employ sealed electrical motors and electrical connections. Metal corrosion is also more likely in these protic solvents.

CONCLUSIONS

Aqueous ethanol may be a useful ice core drilling fluid in warm ($\geq$-25°C) bore holes and where density overturn is not a problem, that is, in holes of moderate depth with temperative gradients of $\leq$2°C per 100 m. The viscosity properties of aqueous ethanol are vastly superior to those of ethylene glycol solutions, even at -55°C, and workable for shallow to moderate depth (<1000 m) bore holes. Definitive tests will have to be performed on trace metal problems because of potential minor corrosion of the drill string by alcohol and by water. Further tests with mechanical drilling systems are necessary to prove the concept since the bulk of drilling experience is with thermal drills.

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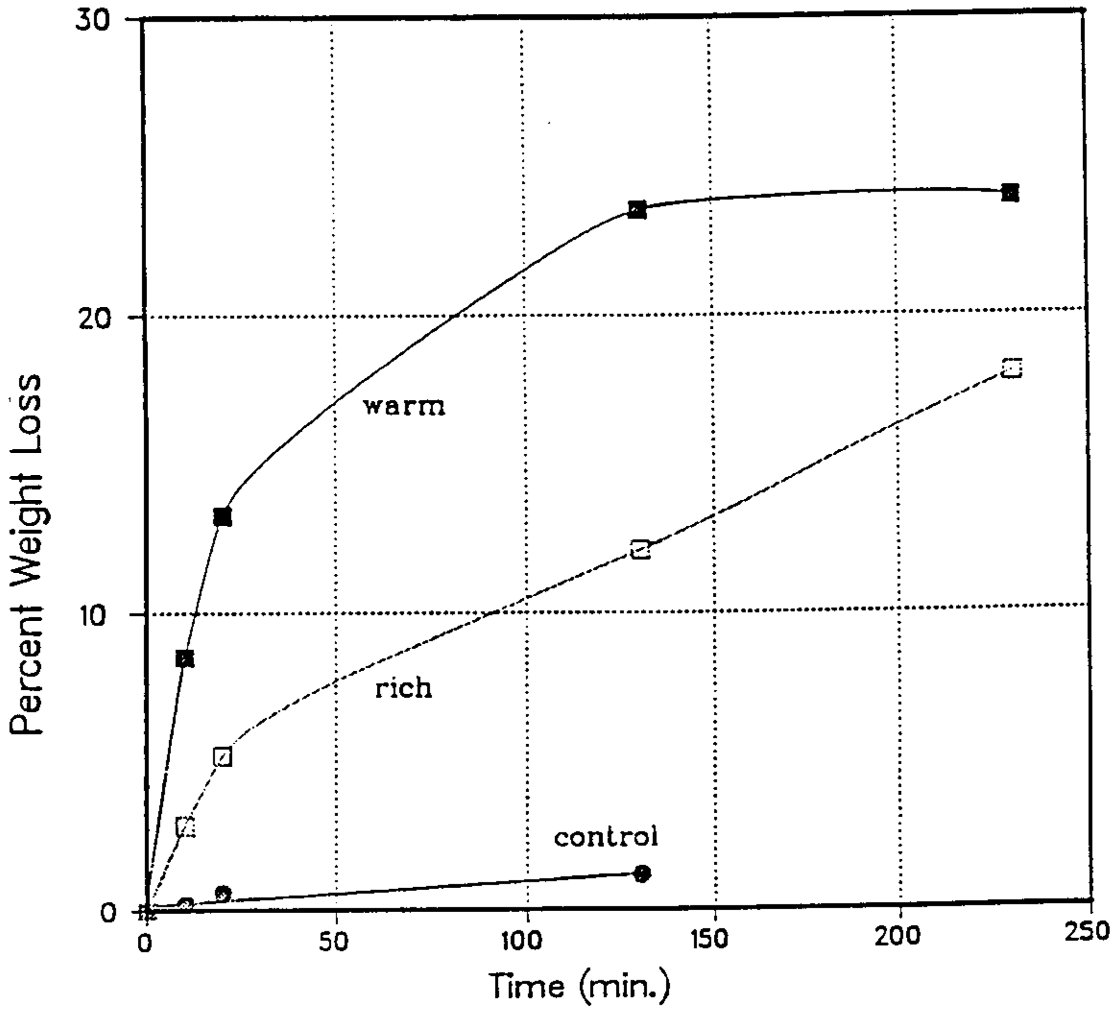

Figure 1. Attack of ice by aqueous alcohol warmer or richer than equilibrium conditions.

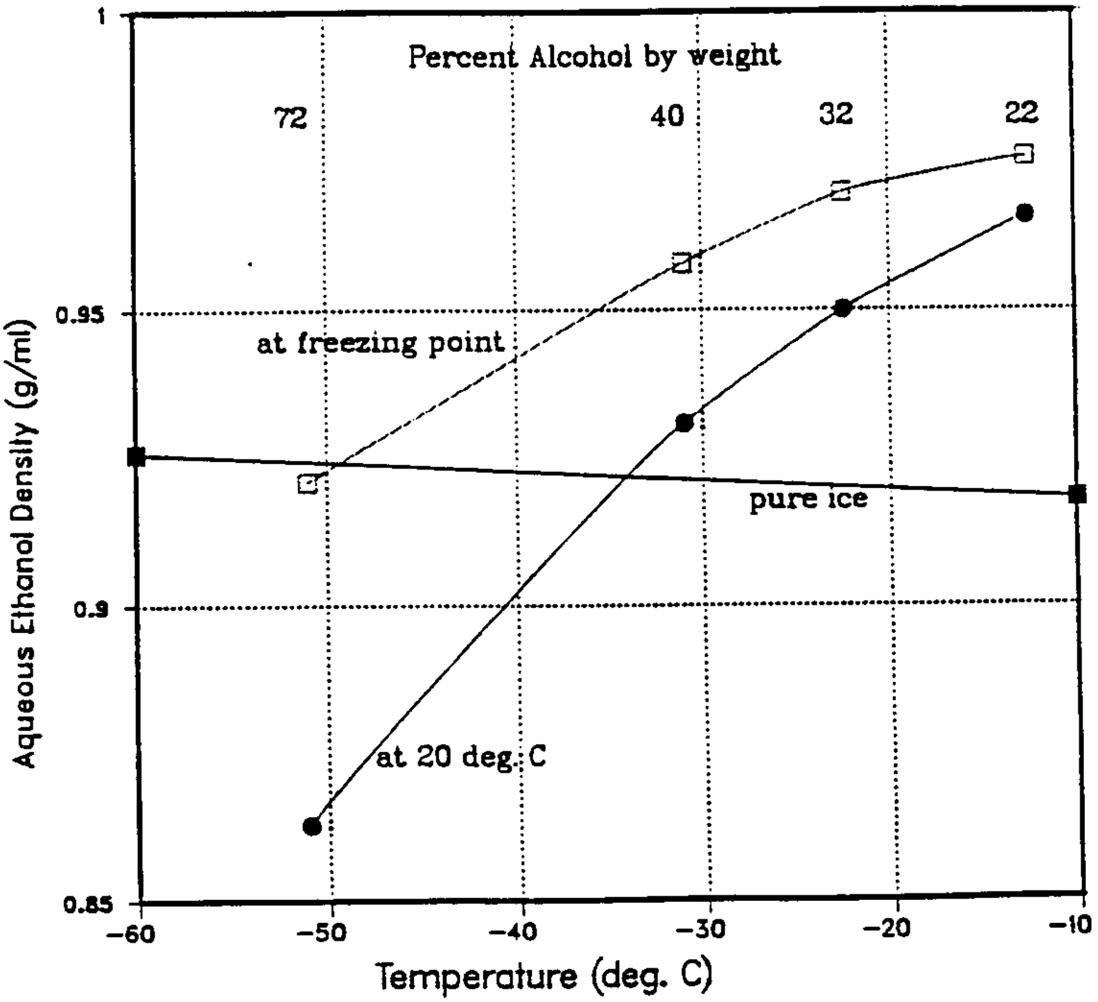

Figure 3. Density of aqueous ethanol solutions at their freezing point. (Percent alcohol content by weight is shown at the top of the figure) The lower curve is hand book data for the density at 20°C.

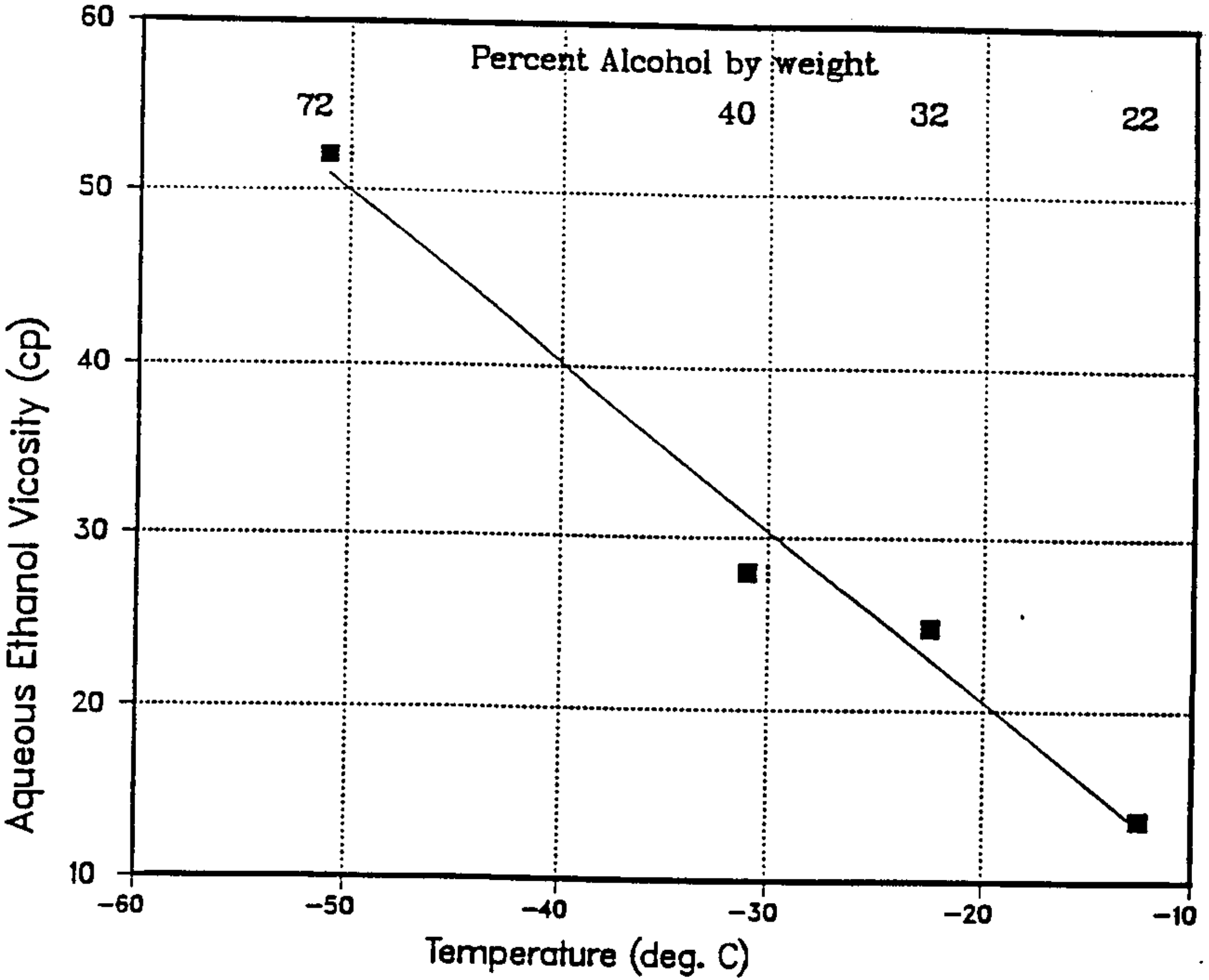

Figure 4. Viscosity of aqueous ethanol solutions at their freezing point. (Percent alcohol content by weight is shown at the top of the figure.)

Table 1. Flash point of ethyl alcohol and aqueous solutions (in comparison with other fluids).

Percent Alcohol	Flash Point (°C)
100	10
50	22
30	28
(Butyl Acetate)	29
(Fuel Oil)	~ 66