

The surface chemistry of chloroform as an extreme-pressure lubricant additive at high concentrations

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Carbon tetrachloride is an extremely good extreme-pressure (EP) lubricant additive at low concentrations (< 3 wt% chlorine) since it can react to form a high-melting-point Fe_3C anti-seizure layer. In contrast, small hydrogen-containing additive molecules (CH_2Cl_2 , CHCl_3) decompose to form FeCl_2 which melts at ~ 940 K and limits the maximum seizure load to ~ 3500 N as measured in a pin and v-block apparatus. However, both thermodynamic calculations and results of a Mössbauer analysis of an iron foil heated in CHCl_3 at 830 K indicate that iron carbide can be formed from chloroform. In addition, it is also found in that case that a plot of seizure load versus concentration, after initially forming a plateau, once again increases with higher additive concentrations (> 4 wt% chlorine) in accord with the idea that a higher melting point carbide film can be formed. It has been shown previously that asymptotes in the plot of removal rate versus applied load correspond to melting of the interfacial anti-seizure film. When using 9.0 wt% chlorine from chloroform as the additive, a drastic increase in removal rate is found at an interfacial temperature of ~ 940 K corresponding to the melting of FeCl_2 and an additional asymptote is evident at ~ 1500 K due to the melting of Fe_3C in accord with the thermodynamic and Mössbauer results.

Keywords: chloroform; extreme-pressure lubrication; additives; surface chemistry

1. Introduction

A model has been developed for the operation of chlorinated hydrocarbon extreme-pressure (EP) lubricant additives which postulates that the additive thermally decomposes at the hot (~ 900 K) lubricated interface to form an anti-seizure layer that consists of FeCl_2 and incorporates small (~ 50 Å diameter) carbon parti-

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cles [1–9]. This lubricating layer ultimately fails when the interfacial temperature reaches the melting point of iron chloride (FeCl_2), and since the interfacial temperature rise is proportional to the applied load, this leads to a behavior in which a plot of seizure load versus additive concentration, measured using a pin and v-block apparatus, reaches a plateau. This model successfully describes the tribological behavior of both chloroform (CHCl_3) and methylene chloride (CH_2Cl_2). In contrast, when carbon tetrachloride (CCl_4) is used as a lubricant additive, surface temperatures are attained which drastically exceed the melting point of FeCl_2 and, in this case, although iron chloride is the extreme pressure lubricant layer at low loads [10–13], at higher applied load (and surface temperatures) this role is played by iron carbide, Fe_3C [14]. Evidence for this comes from both analyses of iron samples that had been reacted in CCl_4 vapor at high temperatures, where Mössbauer spectroscopy clearly reveals the presence of iron carbide, and also from experiments using a pin and v-block apparatus [14]. Measurement of the film formation kinetics for various chlorinated hydrocarbons reveals that films grow more rapidly from CCl_4 decomposition than when either CHCl_3 or CH_2Cl_2 are used [10]. However, the initial film growth rate from chloroform is first order in CHCl_3 pressure, so that increasing the concentration of the additive should result in a concomitant increase in the rate of film deposition and therefore possibly facilitate the transition from iron chloride to iron carbide forming the anti-seizure layer in this case. The results presented in this paper explore this idea and probe the nature of the surface formed by the thermal decomposition of chloroform at high temperatures.

2. Experimental

The apparatus used to carry out these experiments has been described in detail elsewhere [11,12]. Briefly, films were formed on iron foils by reaction in an evacuable cell (operating at a base pressure of 1×10^{-7} Torr) where the foils were suspended on the end of a quartz fiber. The sample is located inside a tube which is enclosed in a furnace and the temperature is controlled and monitored by means of a thermocouple placed in a well inserted into the end of the tube. The chloroform (Aldrich, 99%) is transferred from the bottle into a glass vial which is connected directly to the vacuum system and which is purified by several freeze–thaw–pump cycles. After reaction, the sample is removed and stored in an evacuated desiccator until it is analyzed using Mössbauer spectroscopy. Mössbauer spectra were recorded on a constant acceleration spectrometer model MS-1200D from Ranger Scientific using a ^{57}Co source in a rhodium foil purchased from Dupont Merck Pharmaceutical Company. All spectra were collected at room temperature and isomer shifts are quoted relative to iron metal at room temperature.

Film removal rates are measured using the pin and v-block apparatus as described elsewhere [7]. In this case, the pin (consisting of SAE 3135 steel) and the v-block (consisting of AISI 1137 steel) are immersed in the model fluid consisting

of the chlorinated hydrocarbon (here chloroform; 9.0 wt% chlorine) dissolved in a poly α -olefin (PAO). Removal rates, i.e., wear rates, are measured, after operating the apparatus at a constant load for 600 s, by measuring the width of the wear scars on the faces of the v-block. A simple geometrical calculation yields the amount of wear (which is proportional to the wear rate) directly [7]. The apparatus can also record the torque required to rotate the pin at a constant velocity (290 rpm, which leads to a relative tangential velocity of 9.6 cm/s) for a particular load and so also can be used to measure the interfacial coefficient of friction as a function of applied load [15]. This parameter is required to correctly measure the interfacial temperature (see below).

3. Results

As suggested above, the transition from FeCl_2 to Fe_3C forming the interfacial anti-seizure layer may depend on the surface film growth kinetics and postulates that, if the halide growth rate is sufficiently fast, the additive may be capable of operating at higher applied loads since iron carbide (which has a much higher melting temperature than iron chloride) may then provide the anti-seizure layer. In order to establish whether this idea is feasible, thermodynamic calculations were carried out to establish whether carbide formation from chloroform was thermodynamically allowed. Fig. 1 plots the mole fractions of FeCl_2 , carbon and iron car-

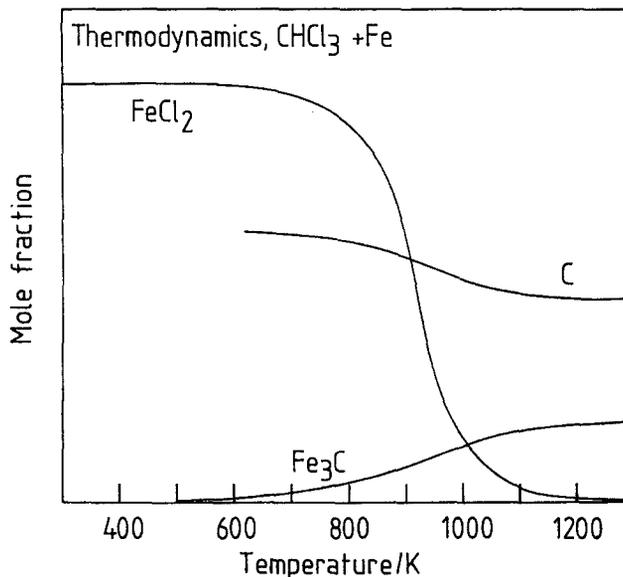


Fig. 1. Plot of the thermodynamically predicted product distribution for the reaction of chloroform with excess iron as a function of reaction temperature.

bide in the layer, calculated from their thermodynamic properties, formed at equilibrium by reaction between CHCl_3 and excess iron. These results were calculated using a standard software package [16]. This shows that, as found experimentally, iron chloride and carbon formation are the thermodynamically preferred reaction products at low temperature (<900 K). As the temperature increases to ~ 950 K, solid iron chloride formation becomes thermodynamically less favored (it melts) and concomitantly the formation of iron carbide becomes more thermodynamically favored. These results suggest that it is feasible to use chloroform as an additive for the formation of a higher-melting-point iron carbide anti-seizure layer.

This idea was further tested by measuring the seizure load versus additive concentration up to higher chloroform concentrations and the results are displayed in fig. 2 which also shows data for carbon tetrachloride for comparison. For low additive concentrations, the plot of seizure load versus additive concentration shows a plateau. It has been demonstrated that the interfacial temperature rise is proportional to the applied load (ref. [7], and see below) and the load at which the plateau occurs corresponds to the melting point of FeCl_2 . In these experiments, the temperature at the interface was calibrated from a variation in seizure load as a function of the bath temperature (T_0 in eq. (1) below) assuming that seizure occurred at a fixed temperature corresponding to the melting of the lubricating film. This

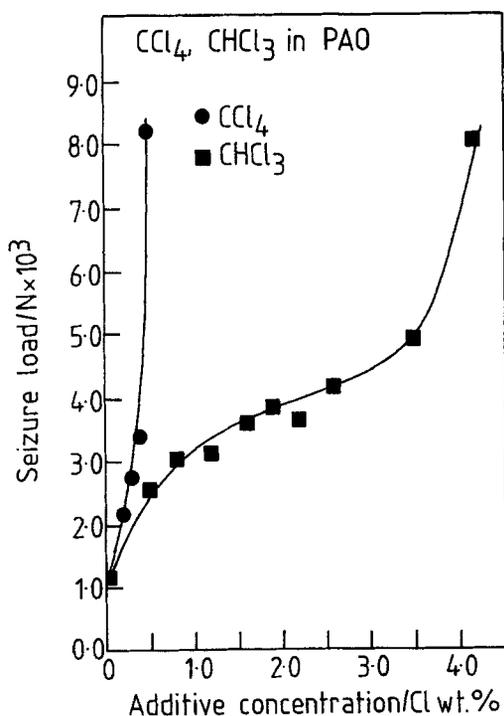


Fig. 2. Plot of seizure load versus additive concentration measured using the pin and v-block apparatus when using CCl_4 (●) and CHCl_3 (■) as additives dissolved in a poly α -olefin (PAO).

allows both the variation of temperature at the interface as a function of the applied load as well as the melting temperature of the interfacial film to be measured.

The data of fig. 2 show that, at additive concentrations above ~ 4 wt%, the seizure load increases once again so that at loads above 3000–4000 N the interfacial temperature is higher than the melting point of FeCl_2 . In the corresponding plot of seizure load versus additive concentration when CCl_4 is used as additive, the seizure load increases extremely rapidly with additive concentration and shows no evidence for the appearance of a plateau. In this case it has been demonstrated that FeCl_2 forms the lubricant layer at low loads, but at higher loads, iron carbide is formed [14].

In order to test whether iron carbide is indeed reactively formed by chloroform decomposition on iron, an iron foil was heated in 55 Torr of chloroform at 830 K for 2 h. The sample was analyzed using Mössbauer spectroscopy which revealed the presence of FeCl_2 . Other peaks are evident, corresponding to about 15% of the total sample, with an isomer shift $\delta = 0.19$ mm/s and $H_{\text{int}} = 20.8$ T, which are characteristic of cementite, Fe_3C [17,18].

As mentioned above, asymptotes in the removal rate versus applied load curve have been shown to correspond to melting of the interfacial film present on the surface. A curve of removal rate versus applied load is shown in fig. 3 when using 9.0 wt% of chlorine from chloroform, corresponding to the high seizure load regime in fig. 2. This curve plots the volume of material removed in 600 s versus the applied load. The solid circles correspond to the removal rate scale shown and the data represented by open circles have been divided by 20. Asymptotes are clearly evident in this curve at applied loads of ~ 400 kgf and at ~ 759 kgf. The applied load L can be related to the interfacial temperature T using the formula [7]:

$$T = T_0 + 2.2 \pm 0.2\mu L, \quad (1)$$

where L is the applied load, μ the interfacial coefficient of friction and T_0 the ambient lubricant temperature. The interfacial coefficient of friction is measured from the slope of the torque versus load curve which is shown in fig. 4 and which varies linearly with applied load up to 750 kgf indicating a constant coefficient of friction over this temperature range. Note that the torque measured at an applied load of 800 kgf increases drastically to a value of 1.1 kgf m, an effect that has been noted also at a similar load when CCl_4 was used as an additive [14]. Measurement of the slope of this curve yields a constant coefficient of friction of $(7.05 \pm 0.2) \times 10^{-2}$ [15] and the interfacial temperature measured from eq. (1) using this value is plotted as the top abscissa on fig. 3.

4. Discussion

The temperatures at the asymptotes of the removal rate versus applied load curve have been shown to correspond to the melting of the interfacial material

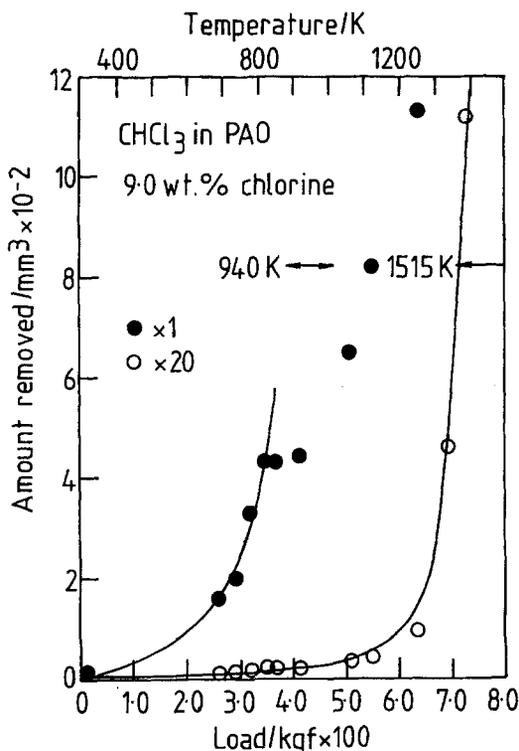


Fig. 3. Plot of the amount of material removed from the surface of the v-block in 600 s versus the applied load in the pin and v-block apparatus for a lubricant consisting of CHCl_3 dissolved in PAO using 9.0 wt% chlorine.

[19,20]. This can be easily understood since the removal rate of a liquid from a surface under the influence of a shear force is infinite. The data of fig. 3 allows these temperatures to be read directly using the calibration made from eq. (1) and the data from fig. 4 and correspond to interfacial melting temperatures of 950 ± 50 and 1450 ± 50 K. Plotted also on this curve are the melting temperatures of FeCl_2 (~ 940 K [21]) and the melting/decomposition temperature of Fe_3C (1515 K [22]) and the horizontal bars indicate the error associated with the measurement. The first asymptote in the plot of removal rate versus load curve therefore corresponds to the melting of FeCl_2 at an applied load of ~ 400 kgf in accord with the behavior of CHCl_3 as a lubricant additive at low concentrations. In addition, the second asymptote corresponds to the decomposition temperature of Fe_3C . This result is in accord with the chemistry that is observed for the thermal decomposition of chloroform on an iron foil at 830 K since the Mössbauer spectrum corresponds exactly to that found for iron carbide. These results indicate that the increase in seizure load found when high concentrations of chloroform are added to PAO (fig. 2), where the interfacial temperature in this region exceeds the melting temperature of FeCl_2 , is due to the formation of Fe_3C which melts at a much higher temperature.

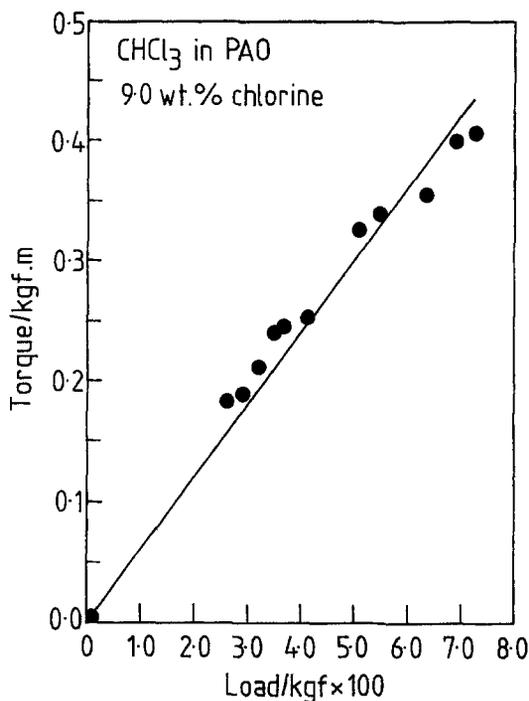


Fig. 4. Plot of torque versus applied load measured using the pin and v-block apparatus when using CHCl_3 dissolved in PAO at a concentration of 9.0 wt% chlorine. This result corresponds to a coefficient of friction $\mu = 0.07$.

Interestingly, this is just the result expected from thermodynamic calculations (fig. 1) and suggests additionally that this type of calculation may prove very useful in general in predicting the behavior of extreme-pressure lubricant additives.

5. Conclusions

Chloroform, when present in low concentrations in PAO, performs as an extreme-pressure additive by forming an anti-seizure film that consists of FeCl_2 and which also incorporates small carbon particles. As the concentration increases, the surface chemistry changes so that Fe_3C forms. The interfacial melting temperature therefore increases substantially allowing the anti-seizure behavior to persist at higher applied loads. This behavior is exactly that predicted thermodynamically so that this might provide a useful strategy for generally predicting the behavior of extreme pressure lubricant additives.

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References

- [1] D. Tabor, *J. Lubrication Technol.* 103 (1981) 169.
- [2] H. Nakai and N. Kanda, *Proc. JSLE Int. Tribology Conf.* 2 (1985) 515.
- [3] R.W. Mould, H.B. Silver and R.J. Syrett, *Wear* 22 (1973) 269.
- [4] A. Dorinson, *ASLE Trans.* 16 (1973) 22.
- [5] R.W. Mould, H.B. Silver and R.J. Syrett, *Wear* 26 (1973) 27.
- [6] D.L. Clason, *Lubr. Sci.* 1 (1989) 281.
- [7] P.V. Kotvis, L.A. Huevo and W.T. Tysoe, *Langmuir* 9 (1993) 467.
- [8] L.A. Huevo, C. Soto, C. Crumer and W.T. Tysoe, *Langmuir* 10 (1994) 3571.
- [9] L.A. Huevo, P.V. Kotvis, C. Crumer, C. Soto and W.T. Tysoe, *Appl. Surf. Sci.* 78 (1994) 113.
- [10] P.V. Kotvis, L.A. Huevo, W.S. Millman and W.T. Tysoe, in: *Surface Science Investigations in Tribology*, eds. Y.-W. Chung, A.M. Homola and G.B. Street (American Chemical Society, Washington, 1992).
- [11] P.V. Kotvis, W.T. Tysoe and M.N. James, *Wear* 153 (1992) 305.
- [12] P.V. Kotvis, L.A. Huevo, W.S. Millman and W.T. Tysoe, *Wear* 147 (1991) 401.
- [13] P.V. Kotvis and W.T. Tysoe, *Appl. Surf. Sci.* 40 (1989) 213.
- [14] P.V. Kotvis, J. Lara, K. Surerus and W.T. Tysoe, *Wear*, submitted.
- [15] F.A. Faville and W.A. Faville, *Lubric. Eng.* 24 (1968) 349.
- [16] HSC Chemistry, Outokumpu Research.
- [17] M. Ron, H. Shechter, A.A. Hirsch and S. Niedzwiedz, *Phys. Lett.* 20 (1966) 48.
- [18] P.M. Gielen and R. Kaplow, *Acta Metall.* 15 (1967) 49.
- [19] E. Rabinowicz, *Friction and Wear of Materials* (Wiley, New York, 1965).
- [20] H. Ernst and M.E. Merchant, *Proc. Special Summer Conference on Friction and Surface Finish*, MIT Report 15 (1940) 76.
- [21] J.C. Weast, ed., *CRC Handbook of Physics and Chemistry* (CRC Press, Boca Raton, 1968).
- [22] I. Barin, *Thermochemical Data of Pure Substances* (VCH, Weinheim, 1989).