

MASTER

CHEMICAL AND OPTICAL STUDIES OF HEAT TRANSFER FLUIDS
CONTAINING SOLAR ENERGY ABSORBERS

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INTRODUCTION

The heat transfer fluid plays an important function in any practical solar-thermal system. In most such systems, heat is transferred from the receiver to the fluid by conduction across a solid-fluid interface. Several recent studies [1] have established that direct absorption of the solar energy into a "black" working fluid is a more efficient process. Most commercially available heat transfer fluids are transparent, however, in significant portions of the solar spectrum. Consequently, the absorptivities of these fluids must be improved by suspension or solution of chromophoric materials.

The purpose of the present study is to enhance the absorptivities of potential heat transfer fluids to solar radiation. Quantitative measurements were made of the increase in "absorptivity" of the fluids to dissolved chromophoric materials. Some previous studies have been made of soluble and insoluble chromophores in aqueous solution [2]. The heat transfer fluids chosen for this study had the following properties: liquid at ambient temperature, transparent to most of the solar spectrum, and low vapor pressure above the boiling point of water. Such liquids are generally commercially available organic and inorganic heat transfer fluids with potential application to mid-range solar thermal devices ($T_{\max} < 350^\circ$). Only chromophoric materials were considered which were soluble in the liquid.

EXPERIMENTAL

All heat transfer fluids were obtained from their commercial source and used without further purification. Therminol 66, MCS-210, and OS-124 were obtained from Monsanto Corp., X2-1163 an experimental silicone oil from Dow-Corning Corp., dixylytethane from Gulf Chemical, and normal hexyl carborane (NHC) from Callery Chemical Co. The chromophores used were either purchased from Alpha Inorganics or donated by various researchers and used without further purification. Ultraviolet, visible, and near

infra-red spectra were recorded on a Hitachi EPS-3T double beam recording spectrophotometer at ambient temperature. The thermal-cycling of both the heat transfer fluids and the fluid plus chromophore solutions was carried out under an argon atmosphere after the solutions had been degassed by flowing argon for a minimum of 15 minutes. Temperature measurements were made using a chromel-alumel thermocouple in the heating oven.

ANALYSIS OF DATA

The evaluation of the chromophoric material as a solar energy absorber was made according to the relationship of Drotning [3].

$$A_m(X,C) = \frac{\int S_m(\lambda)[1-e^{-\epsilon X C}]d\lambda}{\int S_m(\lambda)d\lambda}$$

where

$A_m(X,C)$ is the fraction of the solar energy absorbed by a chromophoric material in a fluid layer of thickness $X(\text{cm})$ and concentration C , (molar) averaged over the solar spectrum of air mass M . $S_m(\lambda)$ is the spectral distribution of the solar intensity through an air mass, m . The quantity $[1-e^{-\epsilon X C}]$ represents the energy attenuation of an optical beam by the chromophore alone, because all spectra were obtained in the double beam mode with the solvent placed in the reference cell. The $A_m(X,C)$ for the heat transfer fluid was obtained from the absorption spectrum for each fluid diluted by a suitable solvent such as CCl_4 , by use of the double-beam spectrometer. The total $A_m(X,C)$ for the fluid layer is the sum of the $A_m(X,C)$ chrom. + $A_m(X,C)$ fluid, because the absorption spectra of the various chromophores and fluids do not overlap.

Inherent in the above treatment are several simplifying assumptions: (1) no abnormal reflectance losses in the spectrometer cell caused by the chromophore in the solvent; and (2) the Beer-Lambert relationship holds for all optical densities.

RESULTS AND DISCUSSION

A listing of all the heat transfer fluids examined in this study, Table I, together with several of their physical properties illustrates the various types of fluids available. After preliminary thermal cycling tests, Therminol 66 was judged to have the best combination of thermal stability, availability, and modest cost. This fluid, a modified terphenyl, exhibited only a slight yellowing after continuous heating for five days at 340°C in an argon atmosphere. The four and five membered polyphenyl ethers MCS-210 and OS-124 both darkened significantly at temperatures much lower than their literature values suggested. The silicone oil X2-1163 decomposed above 250°C and the Gulf DXE while being thermally stable, boils at ~300°C. The normal hexyl carborane was judged too costly to use as a routine solvent for the testing of all of the available chromophores.

Because of the apparent preference for Therminol 66, all the chromophoric materials were tested for thermal stability in this fluid at temperatures between 300°-330°C for a minimum of 3 hours. Several chromophores were heated in Gulf DXE also and demonstrated that thermal stability of the chromophore was independent of solvent. As in the case of the heat transfer fluids, the chromophoric materials tested, Table 2, are by no means an exhaustive list of available candidates but are representative of classes of chemical compounds. The chromophores were chosen by availability and a potential for thermal stability based on known physical properties such as melting point and thermal stability. Absorbers for various regions of the solar spectra were sought by variations in the transition metals, types of ligands, and complexity of the molecules. The results of the thermal cycling tests, Table II, seemed to indicate no a priori method for predicting the thermal stability of the chromophore in solution.

Values of $A_m(X,C)$ were numerically integrated by use of a digital computer for each thermally stable chromophore and each heat transfer fluid, as described previously. Values of $A_m(X,C)$ vs. optical density (concentration

times fluid layer thickness) are plotted in Figures 1 and 2 for the organometallic and organic chromophoric materials respectively, while Figure 3 represents $A_m(X,C)$ vs. optical density for each heat transfer fluid. A discussion of several points concerning these plots is in order. First, calculations of the $A_m(X,C)$ values for the chromophores are based on ambient temperature spectra for the various compounds. Because position and intensity of absorption peaks are generally temperature dependent, a more accurate calculation would use the spectral data at high temperatures; however, temperature increase would also produce "vibrational broadening" of the absorption peak, so that the overall effect on the chromophore may not be too significant. Second, the absorption data used in the calculations were only measured from 0.34 μm to 2.5 μm . No attempt was made to measure the ultraviolet or for infrared spectral regions because these regions contain less than 2% of the solar spectral energy [4]. Finally, the calculations assume an ideal Beer's law relationship, increasing absorption directly proportional to increasing concentration of chromophores. At very high chromophore concentration, there may be some deviation from the ideal.

The results from Figures 1 and 2 illustrate graphically that, as expected, the dark blue and purple colored dyes and complexes (Cr(acac)₃, Calco Oil Blue N) are much more efficient solar energy absorbers than the orange ferrocene compounds or the yellow cobalt complex. An ideal solar absorber should not only have large extinction coefficients for its absorption peaks, but more importantly it should have a non-zero extinction coefficient at all high-intensity solar spectral wavelengths. Since the optical density of the fluid layer is the product of layer thickness and chromophore concentration, the limiting value $A_m(X,C)$ for each fluid layer can be reached by varying either. Ultimately, the type of solar collector, cost of chromophore and fluid and the limiting solubility of the chromophore in the particular fluid will determine the most cost effective method to obtain a high optical density.

The interpretation of Figure 3 indicates little variance among the fluids as solar absorbers. Calculations using the data of the graph

demonstrate that a 10 cm layer of the various pure fluids absorb between 12% and 25% of the available solar energy. Gulf DXE is the most efficient at 25%, MCS-210 the least efficient at 12%, while the remaining four are all clustered around 19% efficiency. An addition of a small quantity of the proper dye or metal complex increases the total direct absorptivity of solar energy to ~85%.

Further studies in this program will determine the photochemical stability of the various fluids and chromophores as a function of time and temperature. Eventually, we plan to use the results obtained in these studies to design and synthesize more thermally and photochemically stable heat transfer fluids, incorporating highly efficient solar absorbers.

LIST OF FIGURES

- Figure 1 $A_m(X,C)$ for Various Organometallic Compounds vs. Log Optical Density
- Figure 2 $A_m(X,C)$ for Organic Dyes vs. Log Optical Density
- Figure 3 $A_m(X,C)$ for Various Heat Transfer Fluids vs. Log Optical Density

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TABLE I

HEAT TRANSFER FLUIDS

<u>Fluid and Company</u>	<u>Type</u>	<u>Empirical Formula</u>	<u>Boiling Pt.</u> °C	<u>Viscosity</u> Cst. (°C)	<u>Density</u> g/ml (°C)	<u>Price</u> \$/gal
Therminol 66 (Monsanto)	Modified Terphenyl	$\sim C_{18}H_{22}$	decomp. (350-360)	30(38°)	0.995(38°)	\$ 8.00
Dixylylethane (DXE) (Gulf)	Dixylyl Substituted Ethane	$C_{18}H_{22}$	(322-324)	$\sim 12.8(38^\circ)$	0.978(16°)	\$ 7.00
MCS-210 (Monsanto)	Polyphenyl Ether	$C_{24}H_{18}O_3$	Similar to OS-124	Similar to OS-124	Similar to OS-124	Similar to OS-124
OS-124 (Monsanto)	Polyphenyl Ether	$C_{30}H_{22}O_4$	528°C est.	363(38°)	1.2(20°)	\$1200.00
X2-1163 (Dow-Corning)	Polydimethylsilicone	$(C_2H_6Si-O)_x$	Decomposes above 200°C	20(25°)	0.946(25°)	\$ 26.00
N-Hexylcarborane (Callery Chem.)	Substituted Carborane	$B_{10}C_8H_{24}$	(288-360) est.	-	$\sim 0.9(20^\circ)$	\$2000.00

Table II

THERMAL STABILITY OF CHROMOPHORES^(a)

Compound	Empirical Form	Color	Temp. (°C)	Time at Tmax (hrs.)	Thermally Stable
Cr(acetylacetonate) ₃	C ₁₅ H ₂₁ O ₆ Cr	Purple	318	5 1/2	Yes
Diferrocenyl	C ₂₀ H ₁₈ Fe ₂	Orange	334	3	Yes
1,1-Bis (3,3,3 Triphenyl -1, 1- Dimethyl-disiloxanyl) ferrocene	C ₅₀ H ₅₀ Si ₄ O ₂ Fe	Orange	333	3	Yes
1,1-Bis (Tridodecylsilyl) ferrocene	C ₈₂ H ₁₅₈ Si ₂ Fe	Yellow-Orange	324	3 1/2	Yes
Cr(Benzoylacetonate) ₃	C ₃₀ H ₂₇ O ₆ Cr	Purple-Green	330	4	Yes
Co(C ₅ H ₅)(1,2B ₉ C ₂ H ₁₁)	C ₇ H ₁₆ B ₉ Co	Yellow	315	3 1/2	Yes
Calco Oil Blue N	C ₁₈ H ₁₈ N ₂ O ₂	Blue ^(b)	330	4 1/2	Yes
Calco Oil Violet Zirs	C ₂₁ H ₁₅ O ₃ N	Violet ^(b)	332	3	Yes
Calco Nigrosine Base	Proprietary	Black	322	4	No
Fe(Acetylacetonate)	C ₁₅ H ₂₁ O ₆ Fe	Red	321	3 1/2	No
1,1'-Diacetylferrocene	C ₁₄ H ₁₄ O ₂ Fe	Red-Orange	326	4	No
1,1'-Dibenzoylferrocene	C ₂₄ H ₁₈ O ₁ Fe	Red-Orange	333	3	No
1,1'-Bis(Hydroxymethyl)ferrocene	C ₁₂ H ₁₄ O ₂ Fe	Orange	334	4 1/2	No
Bis(cyclopentadienyl)Titanium dichloride	C ₁₀ H ₁₀ Cl ₂ Ti	Red	313	3 1/2	No
Ce(Tetramethyl Heptanedionato) ₄	C ₄₄ H ₇₆ O ₈ Ce	Brown	330	4 1/2	No
Fe(Tetramethyl Heptanedionato) ₃	C ₃₃ H ₅₇ O ₆ Fe	Red	314	3 1/2	No
Fe(C ₅ H ₅)(1,7B ₉ C ₂ H ₁₁)	C ₇ H ₁₆ B ₉ Fe	Dark Green	334	3	No
Ferrocene	C ₁₀ H ₁₀ Fe	Orange	~200	2	Sublime
1,1'-Bis(5-phenyl -1,1-3,3,-5,5- hexamethyl trisiloxanyl) ferrocene	C ₃₄ H ₅₄ Si ₆ O ₄ Fe	Yellow	331	3 1/2	No

^(a) in Therminol 66^(b) Color change (either reaction or isomerization)





