Diffusion interaction and quantitative analysis of zinc dialkyldithiophosphate content in lube base oils in terahertz regime

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Received May 17, 2011; accepted August 10, 2011; posted online October 25, 2011

We investigate the diffusion interaction and quantitative analysis of zinc dialkyldithiophosphate (ZDDP) mixed with lube base oil (LBO) at different concentrations using terahertz time-domain spectroscopy (THz-TDS). When the concentration exceeds 6.78%, the characteristic absorption peaks exhibit a significant shift, and the absorption coefficient peak value is non-linear against concentration. Moreover, the absorption coefficients of mixed samples follow the Beer’s law at a concentration below 6.78%. The quantitative analysis enables a strategy for monitoring the formulation of lubricating oil in real time.

OCIS codes: 070.4340, 160.4760, 190.4400, 300.6495.

doi: 10.3788/COL201109.110010.

Zinc dialkyldithiophosphate (ZDDP), as a multifunctional additive and inhibitor in petroleum industry, works mainly as an antiwear, antioxidant, and anticorrosion agent[1,2]. ZDDP mixed with lube base oils (LBOs) has been used to study the effect of concentration on lubrication boundary and tribological properties[3]. The concentration of ZDDP in LBOs plays a crucial role in formulation, which is a balance of many different aspects of performance. Lubricating formulation generally results from a molecular diffusion mechanism due to the relative motion of molecules. Molecular diffusion in a steady-state and nonequilibrium system is divided into molecular motion and interaction. Molecular motion, containing the electronic motion, molecular vibration, and molecular rotation, is complicated and multibody. The intermolecular and intramolecular modes of ZDDP and LBO determine the ability of the reactants to approach each other and products to separate from each other. The intermolecular and intramolecular interactions often have their characteristic frequencies in the region lower than 100 cm−1.

Two major strategies can be used to investigate low-frequency diffusion between ZDDP and LBO. Femtosecond optical Kerr-effect (OKE) spectroscopy has been used over past decades to investigate molecular motion in liquids and liquid mixtures[4]. The second technique is terahertz time-domain spectroscopy (THz-TDS)[5,6], which is a promising and nondestructive analysis method for petroleum products. A unique attribute of THz-TDS is its ability to sensitive measure the induced molecular dipole moments of many petroleum products. Furthermore, the low photon energy of radiation allows propagation through flammable liquids without any danger of combustion. The past few years have witnessed a remarkable effort in employing THz-TDS for investigating the properties of petroleum products, including gasoline, diesel, lubricating oil, lube base oil, water-oil complexes, and organic solvents[7–9]. The absorption spectra of petroleum products show collective modes in the THz region.

In this letter, we described the interaction between ZDDP and LBO using THz-TDS. First, we measured the THz-TDS of polar liquid of ZDDP at different concentrations in LBO from Russia and calculated their absorption coefficients. We then investigated the usefulness of the standard absorption coefficient by comparing the calculated concentrations and the actual mixing ratios of the ZDDP in LBO from Korea. Investigating the quantitative analysis of lubricating oil formulation is important to find a strategic application in the field of real-time monitoring.

All measurements were performed with a conventional transmission setup for THz-TDS based on a ZnTe emitter for THz generation and electro-optic sampling[10]. The ZDDP used was zinc nbutyl-isooctyl-dithiophosphate without further purification. ZDDP molecules can exist in solution not only as monomers, but also as dimers or even higher order oligomers; the zinc atoms are connected by two bridging DDP groups, and each zinc atom is chelated by one DDP group[11]. The viscosity indices of LBOs from different countries have been studied[12], and the absorption peak positions and spectral shapes of LBO have been shown to correspond very well with previous data. The collected THz-TDS of LBO contain the necessary analytical information to identify the viscosity index, such as spectral variations related to different chain lengths. For liquid spectroscopy, the accuracy of the absorbance and interaction determination depends directly on the precision of the concentration-dependent changes in the THz absorption coefficient. We mea-
sured the THz-TDS of polar liquid of ZDDP mixed with
LBO of viscosity 150 from Russia (ZDDP-Russia150) and
viscosity 70 from Korea (ZDDP-Korea70) at several
concentrations. The interaction between ZDDP and
LBO were devided into two broad categories: frequency
shift and quantitative analysis. The sample in liquid
phase was sealed in a polystyrene (PS) cuvette with a
side thickness of less than 1 mm that is transparent for
visible light. From our measured THz-TDS data, the
transmittance of PS wafer substrate was calculated as
88.66%. Moreover, the empty cuvette was used as the
reference measurement, and no macroscopic bubble was
found in the sample. All the measurements were per-
formed at room temperature and humidity was kept at
less than 3.0%.

Figure 1 shows the THz absorption coefficient $\alpha$ of
ZDDP-Russia150 with a variable concentration range of
0.18% to 20.01%. The vertical axis was offset to clar-
ify with different concentrations. The absorption peaks
shift significantly at the concentration of 20.01%, and
the frequency shifts ($\Delta f$) are 0.073, 0.147, and 0.176
THz for peaks 1, 2, and 3, respectively. As shown in the
inset of Fig. 1, in the ZDDP-Russia150 system, the con-
centration dependence of $\alpha$ follows the Beer’s law in the
concentration range from 0.18% to 6.78%. The intensity
changes of molecular interaction at THz frequency region
are thought of as peak shifts in intramolecular vibrations
and/or the generation and disappearance of the peaks
in direct intermolecular vibrations\(^\text{[11]}\). Thus, the peak
shift in our case is due to the intramolecular vibrations
of alkanes and aromatics in LBOs.

To understand the absorption spectra, calculation was
carried out using the GAUSSIAN 03 software package.
The B3LYP method was used in conjunction with the
6-31G basis set. The hydrocarbons ranging in carbon
number of 20–40 of LBO with different viscosity grades
can be classified into a few broad categories: alkanes,
alkenes, alicyclics, and aromatics. Alkenes are unsatu-
rated molecules and comparatively rare in LBO. The
molecular modes of LBO of viscosity 150 from Russia (ZDDP-Russia150)
are thought of as peak shifts in intramolecular vibrations
and/or the generation and disappearance of the peaks
in direct intermolecular vibrations\(^\text{[12]}\). Thus, the peak
shift in our case is due to the intramolecular vibrations
of alkanes and aromatics in LBOs.

Based on the calculated results at the B3LYP/6-31G level
in the interaction mechanism between ZDDP and LBO.
Figure 2 depicts the frequency-dependent vibrational modes of n-
eicosane, 5-ethyloctadecane, eicosene, 4-ethyloctadecene,
and dibenzo [a, h] pyrene representing alkanes, alkenes,
alicyclics, and aromatics. Absorption peaks of LBO

\[
\alpha(\nu) = \frac{2\pi}{3\nu c^2} \nu^2 [1 - \exp(-\nu h/k_B T)] \\
\times \int_{-\infty}^{\infty} df \exp(-i\nu t) \langle M(t) \cdot M(0) \rangle,
\]

where $c$ is the speed of light, $\nu$ is the angular frequency,
and $k_B T$ has its usual meaning. Two types of molecular
motions in condensed phase contribute to the THz re-
gion: one is the reorientational relaxation of permanent
and induced dipoles of the molecule, the other is the
interaction between solute and solvent, which plays a
role in interpreting the THz spectra. The total dipole
moments of system can be expressed as the sum of the
microscopic dipoles occurring in a liquid sample; the per-
manent and induced dipole moments contribute to the
THz region. ZDDP has short chain structures, whereas
LBO molecules have saturated linear or branched long
chain structures and cyclic structures based on five-
and six-membered rings or benzene rings. As shown at
the right-hand side of Fig. 1, ZDDP dissolved in
LBO is in the form of clusters, and the interaction be-
tween the ZDDP is negligible under the present exper-
imental conditions. More surrounding ZDDP molecules
collide with the LBO continuously in the solution, caus-
ing the increased strength of fluctuations of the dipole

Fig. 1. THz absorbance spectra of ZDDP-Russia150, with
concentration varying in the range of 0.18%–20.01%. The $y$-
axis values have been offset for clarity. The inset shows the
absorption coefficient of peak 1 against concentration, which
follows the Beer’s law at the concentration below 6.78% (solid
line).

Fig. 2. Simulated absorption results of n-eicosane, 5-
ethylodctadecane, eicosene, 4-ethyloctadecene, and dibenzo
[a, h] pyrene.

Located at lower frequency are affected by the motions of
the alkyl chains, and the absorption modes are displayed
as “collective modes”. However, the complicated composi-
tion of petroleum, which is a mixture of organic chem-
icals ranging in size from simple gaseous molecules to
very high molecular weight asphaltic components, shows
that the simulated absorption peaks in Fig. 2 are not
perfectly consistent with experimental results in Fig. 1.
The molecular modes of LBO thus play a crucial role
in the interaction mechanism between ZDDP and LBO.
Based on the calculated results at the B3LYP/6-31G level
and with the aid of visualization of Gaussian View, the
molecular modes of dominant alkanes and aromatics in
the LBO are shown to correspond to collective torsional
and vibrational ones, which give rise to the resonance of
LBO in the 0.2–2.5-THz range.

The THz-TDS corresponds to Fourier transformation of the
time-correlation function of the total dipole momen-
t of the system, $M(t)$, which can be expressed as\(^\text{[13,14]}\)

\[
\alpha(\nu) = \frac{2\pi}{3\nu c^2} \nu^2 [1 - \exp(-\nu h/k_B T)] \\
\times \int_{-\infty}^{\infty} df \exp(-i\nu t) \langle M(t) \cdot M(0) \rangle,
\]
3.489%. The frequency shift occurs more significantly at peak 3 than that at peak 1, with a decrease of interaction strength between the ZDDP and LBO molecules. The concentration of ZDDP in LBO has a significant effect on the performance of lubricating oils under boundary lubrication conditions; thus, ZDDP at lower concentrations (0.1%–5%) could be used in normal engine oils for maximum wear protection[5].

To study the usefulness of the standard absorption coefficients of ZDDP-Korea70, the calculated concentrations from the $\alpha(\nu)$ was compared with the actual mixing ratio from 0.088% to 3.489%. Figure 3 shows the measured absorption coefficient ($\alpha_{\text{obs}}$) of ZDDP-Korea70 as a function of frequency. The two relatively strong absorption peaks at 0.88 and 2.2 THz did not shift with the changes in concentrations. We selected the two peaks as marker bands and plotted the $\alpha_{\text{obs}}$ of those bands against concentration from 0.088% to 3.489%, as shown in the inset of Fig. 3. The adjusted R-squares were 0.838 and 0.973, which correspond to 0.88 and 2.2 THz, respectively. Thus, $\alpha_{\text{obs}}$ increased in close proportion to the concentration, indicating that the Beer’s law can be applied to the present ZDDP-Korea70 system. The outstanding spectral stability of the measurements allowed us to obtain a quantitative analysis of the THz spectra.

To obtain a standard spectrum for quantitative analysis the absorption coefficient $\alpha_{\text{calcd}}$, shown in Fig. 3, of ZDDP-Korea70 was calculated for a certain frequency region based on the $\alpha$ of ZDDP and Korea70 in the 0.5–1.8 THz frequency region, as shown in the inset of Fig. 4[17,18]. Every $\alpha_{\text{obs}}$ shape was well reproduced by $\alpha_{\text{calcd}}$. Figure 4 shows the calculated concentration $C_{\text{calcd}}$ of ZDDP is best reproduced, matching the expected concentration $C_{\text{f}}$ values with adjusted R-square greater than 0.954. The proposed method for real-time monitoring of formulation, in view of the data presented above, helps in the optimization of formulation process.

In conclusion, ZDDP mixed with LBOs of Russia150 and Korea70 at several concentrations are studied using THz-TDS. In the ZDDP-Russia150 system, the absorption peak positions shift significantly at 20.01% concentration. The surrounding ZDDP molecules that collide with LBO in solution cause the frequency shift at picosecond time scale. Moreover, in the ZDDP-Korea70 system, the quantitative analysis of system displays reproducibility, which can be used for real-time monitoring of formulation. All the results indicate that ZDDP is dissolved in cluster form to modulate the nature of lubricating oil, and that the ZDDP-LBO system follows Beer’s law at concentrations below 6.78%. The THz-TDS with data compression techniques can be used to monitor the formulation of lubricating oil in real time.

This work was supported by the Program for New Century Excellent Talents in University (No. NCET-08-0841), the National Natural Science Foundation of China (Nos. 50672132, 60778034, and 60877038), the Research Fund for the Doctoral Program of Higher Education (No. 200804250006), and the State Key Laboratory of Heavy Oil Processing, China University of Petroleum (No. 2008-14).

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