A Study on the Effect of Polyamine on the Adsorption of Asphalt-Like Functionalities onto Silica Surface

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The effect of precoating of silica with polyamine surfactants on the adsorption of five model compounds containing asphalt-like functionalities was studied. Hexadecyltrimethylammonium chloride (HDTMA) and 1-hexadecylamine were used for silica precoating. The model compounds representing five asphalt functionalities were benzoic acid, phenol, benzylbenzoate, benzophenone, and quinoline. All the adsorption isotherms conformed well to the Langmuir adsorption model. All the model compounds showed decreased adsorption with the HDTMA precoating. However, two acidic compounds, benzoic acid and phenol, showed enhanced adsorption on the silica precoated with 1-hexadecylamine. In aqueous solutions, the adsorption of the acidic compounds were in the following order: silica precoated with 1-hexadecylamine > silica precoated with HDTMA > uncoated silica.

Key Words : Adsorption, Polyamine, Asphalt, Silica

1. Introduction

One of the major causes of asphalt pavement failure has long been recognized as the stripping of asphalt cement from the aggregate surface caused by water intercession at the asphalt-aggregate interface[1~6]. Fromm[1] suggested that water droplets migrate through the asphalt film to the base material by spontaneous emulsion. Once the emulsion is formed under an asphalt layer, the separation of the asphalt and aggregate layers begins to occur by the ionization and dissociation of both layers.

There have been many ways to reduce the stripping damage in asphalt pavement. Among them, the addition of antistripping agent (ASA) to asphalt has been a common method of reducing the stripping damage because of its low cost and ease of application[7~9]. However, many ASAs can lose their effectiveness in hot asphalt by interacting chemically and physically with compounds in the asphalt to form inactive complexes[10]. In recent years, precoating of the aggregate with the ASA has been studied for overcoming the

inherent disadvantages of direct application of the ASA to the asphalt.

Adhesive bond of asphalt to the aggregate is important for the durability of asphalt paving mixtures. Therefore, the chemistry at the asphalt-aggregate interface has been the main concerns to understand in view of the bonding between these two materials. Many studies which have investigated the asphalt-aggregate bonding in terms of adsorption of asphalt molecules on to the aggregate surface have been undertaken[11~14].

Peterson[15] identified the chemical functional groups present in asphalt using differential infrared spectrometry with selective chemical reactions. The functional group types include carboxylic acids, phenolics, ketones, sulfoxides, pyrrolics, pyridinics, and others. Polarity of the asphalt is due to the presence of heteroatoms (S, N, O). The heteroatoms are contained in the functional groups.

Plancher et al.[11] founded that polar functionalities in asphalt played an important role in binding by strongly adsorbing to the aggregate surface. Carboxylic acids, the compound type most selectively adsorbed by all type of aggregate was also the compound type most readily displaced by water. Phenylsulfoxide, benzophenone, and phenol were favorably adsorbed onto

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either acidic (granite) or basic aggregate (limestone).

Mathews[7] reported that addition of cationic surfactant as antistripping agents (ASA) to asphalt enhanced adhesion of asphalt to the aggregate surface and effectively reduced the stripping damage due to water. The used cationic surfactants contained long-chain alkyl or alkenyl groups and at least one primary amine group. The action of these surfactant is to migrate to the aggregate surface to render the surface hydrophobic, and to facilitate the adsorption of asphalt onto the aggregate surface. Dybalski[10], however, pointed out that these conventional ASAs containing amine groups can react with acidic compounds in asphalt to form amides that would be inactive with the aggregate surface. In addition, in a typical hot mix, only 30-40% of the surfactant added could migrate to the aggregate surface to be effective due to the high viscosity of the asphalt and short heating time (less than 3 h). For these reasons, a method to apply the ASAs directly to the aggregate surface which is to precoat the aggregate surface before the mixing of asphalt has been proposed.

The objective of the present study was to investigate the effect of precoating of the silica surface with ASAs on the adsorption behaviour of asphalt functionalities on silica surface. The adsorption isotherms of selected model compounds containing typical asphalt-like functionalities were investigated. Antistripping agents containing polyamine groups were used to precoat the silica surface. Also, adsorption experiments of the model compounds were performed in aqueous solutions, and their results were compared with those performed in cyclohexane solution to examine the effect of water on the interfacial bonding between the asphalt and the silica surface.

2. Material and Methods

2.1. Materials

Hexadecyltrimethylammonium chloride [HDTMA, $CH_3(CH_2)_{15}N(CH_3)_3Cl$] and 1-hexadecylamine [$CH_3(CH_2)_{15}NH_2$] were used as polyamine-type antistripping agents and were purchased from Aldrich. Benzoic acid (>99%), phenol (>99%), quinoline (>99%), benzylbenzoate (>99%), and benzophenone (>99%) were selected as model compounds representing typical chemical functionalities in asphalt and were purchased from Aldrich. Cyclohexane (>99%, spectrophotometric grade,

Aldrich) were used as a solvent for the adsorption of the model compounds. Dichloromethane >99%, spectrophotometric grade, Aldrich) was used as a solvent for 1-hexadecylamine and distilled water was used for HDTMA. Moisture contained in the liquid solvent was removed before use by the immersion of type-4A molecular sieves. Silica gel (> 99%, Aldrich) was used as the model substrate representing typical aggregate for the asphalt paving mixtures. Its particle size, pore size, and surface area were 200-425 µm, 150 Å, and 300 m^2/g, respectively. Moisture in the silica gel was removed before use by drying at 120℃ for 24 h.

2.2. Precoating of Silica with ASAs

In order to prepare the precoated silica with HDTMA, it was adsorbed onto silica. From the adsorption rate experiment, it was found that 24h was a sufficient time for the adsorption equilibrium. 500 and 3000 ppm solutions were prepared by dissolving HDTMA in distilled water. 2g of oven-dried silica substrate was added to 100ml of the HDTMA solutions. The solution mixtures were allowed to incubate with constant shaking for 24h in a water bath, which was maintained at 25℃. After adsorption, the samples were filtered through a Teflon filter (0.22µm). The filtered silica was washed with distilled water to remove any weakly adsorbed fraction. Then, the silica was dried at 25℃ for 24h in a vacuum desiccator and used as a precoated silica with HDTMA for the adsorption of model compounds.

For the 1-hexadecylamine, 1h was sufficient for the adsorption equilibrium to occur. Solutions of 1 and 3g/l concentrations by dissolving 1-hexadecylamine in dichloromethane were prepared. 2g of oven-dried silica was introduced into 100ml of each solution and were stirred for 1h in a water bath, which was maintained at 25℃. The rest of the experimental procedures were performed in the same way as those described above for the HDTMA.

2.3. Adsorption of Model Compounds onto Precoated and Uncoated Silica

Solutions of concentrations ranging from 0.25 to 10g/l were prepared by dissolving model compounds in cyclohexane. Then, 2g of silica was added to 100ml of each solution. The solution mixtures were agitated for 1h in a water bath at 25℃. One hour

was sufficient for attaining equilibrium for the adsorption. Samples of 7ml volume were taken before and after adsorption for the analysis. For the adsorption in aqueous environment, two acidic model compounds, benzoic acid and phenol, were dissolved in distilled water. The same procedure as described above for the adsorption in cyclohexane was adopted for the adsorption isotherm experiment in aqueous solutions.

2.4. Analysis

Each sample solution after adsorption was filtered through a 0.22μm Teflon filter to remove all suspended silica particles. All the filtered solutions were analyzed by using an ultraviolet (UV) spectrophotometer (Perkin Elmer Lambda Bio20). The characteristic length for each compound is summarized in Table 1.

UV analysis is based on Beer's law, $A = \varepsilon bc$, where, A, ε, b, and c denote UV absorbance, absorptivity (L/g · cm), cell pathlength (1cm), and solution concentration (g/l), respectively. A calibration curve of each solution was obtained using standard solutions of known concentrations. The concentrations of the sample solutions were determined by reading the calibration curve at the measured absorbance.

3. Results and Discussion

3.1. Adsorption of Model Compounds on Uncoated Silica and Precoated Silica with HDTMA

Five model compounds were adsorbed onto uncoated silica and precoated silica with HDTMA in cyclohexane solution at 25℃ and their results were compared as can be seen in Fig. 1, 2, 3, 4, and 5. All the adsorption isotherms were analyzed after the adsorption equilibria had been attained, using initial concentrations ranging 0.15 to 10g/l.

Fig. 1[6] shows the adsorption isotherms of benzoic

Table 1. Wavelength of UV maxima of model compounds in water and cyclohexane solutions

Sample Compound	Solvent	Wavelength
Benzoic acid	Cyclohexane	275
Phenol	Cyclohexane	272
Benzophenone	Cyclohexane	250
Quinoline	Cyclohexane	274
Benzylbenzoate	Cyclohexane	275
Benzoic acid	Water	273
Phenol	Water	270

acid. Adsorption increased quickly at low concentrations and formed a plateau at high concentrations, featuring the Langmuir type adsorption behaviour. Benzoic acid adsorbed more to the uncoated silica than to the precoated silica with HDTMA. As the precoating amount of HDTMA increased, the adsorption amount decreased. Benzoic acid can be adsorbed to the silanol groups of the silica surface through hydrogen bonding. However, precoating of silica with HDTMA could inhibit the interaction between the silanol groups of the silica surface and benzoic acid. Consequently, benzoic acid adsorbed to only a small portion of the unoccupied adsorption sites on the silica surface, causing the decrease in the adsorption amount. Phenol showed similar adsorption behavior to that of benzoic acid as shown in Fig. 2[6]. Phenol is also an acidic compound and can be adsorbed to the
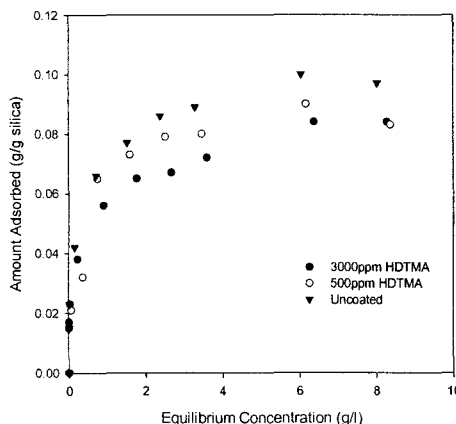

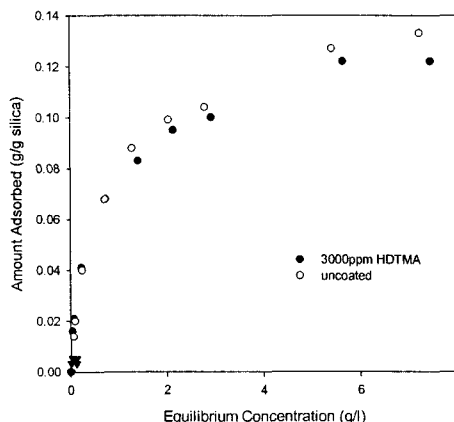Fig. 1. Adsorption isotherms of benzoic acid on uncoated and HDTMA silica.

Fig. 2. Adsorption isotherms of phenol on uncoated and HDTMA silica.

silanol groups of the silica surface through hydrogen bonding. Therefore, the decrease of the adsorbed amount on the precoated silica with HDTMA can be attributed to the same factors as those described for benzoic acid.

As shown in Fig. 3, 4, and 5, adsorption amount of nonacidic compounds also decreased with the silica precoated with HDTMA. This also due to the fact that preoccupied HDTMA on the silica surface decreased adsorption sites available for the nonacidic compounds. However, they showed a certain level of adsorption amount because of the van der waals interaction between the long carbon chain of HDTMA and the adsorbing organic model compounds. All the adsorption behaviour were well fitted to the Langmuir adsorption isotherms.
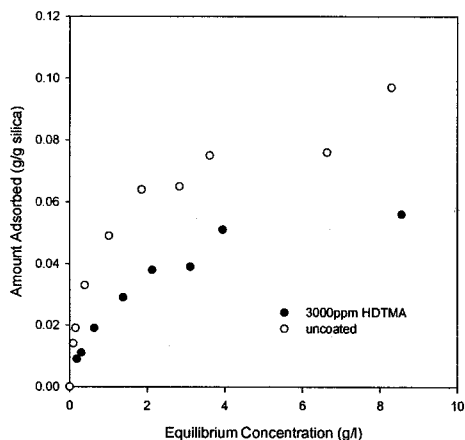

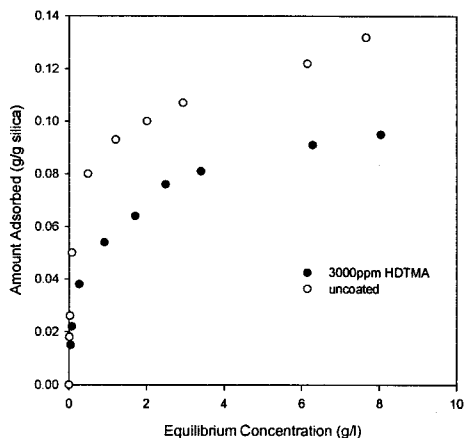Fig. 3. Adsorption isotherms of benzylbenzoate on uncoated and HDTMA silica.

3.2. Adsorption of Acidic Model Compounds on Uncoated Silica and Precoated Silica with 1-hexadecylamine

Two acidic model compounds (benzoic acid and phenol) were adsorbed onto the silica precoated with concentration of 3g/l of 1-hexadecylamine in cyclohexane solution at 25℃. The adsorption results were compared with those for the uncoated silica as can be seen in Fig. 6 and 7[6]. For the adsorption isotherms of benzoic acid, adsorption increased quickly at low concentrations and attained a plateau at high concentrations, featuring Langmuir-type adsorption behaviour. In contrast, the adsorption isotherms of phenol showed a continual increase over the high concentration range.

As illustrated, both benzoic acid and phenol adsorbed more to the precoated silica with 1-hexadecylamine than to the uncoated silica. The higher initial slopes of the adsorption isotherms for the precoated silica relative to those for the uncoated silica suggest that benzoic acid and phenol have a higher adsorption affinity toward the precoated silica. Amino groups have free electron pairs and thus, can act as Lewis bases, i.e., proton acceptors or electron pair providers[3]. Acidic functionalities such as benzoic acid and phenol can transfer a proton to a basic amine groups of 1-hexadecylamine. Therefore, the acidic molecule is negatively charged while the amino group has a positive charge by forming a quarternary ammonium ion. As a result, electrostatic attraction occurs between the acidic molecule and the ammonium ion. This acid-base interaction can explain the enhancement
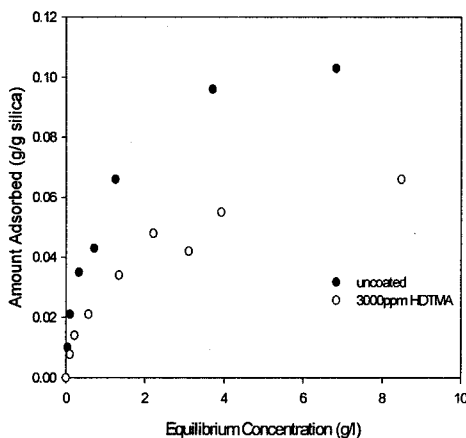

Fig. 4. Adsorption isotherms of quinoline on uncoated and HDTMA silica.

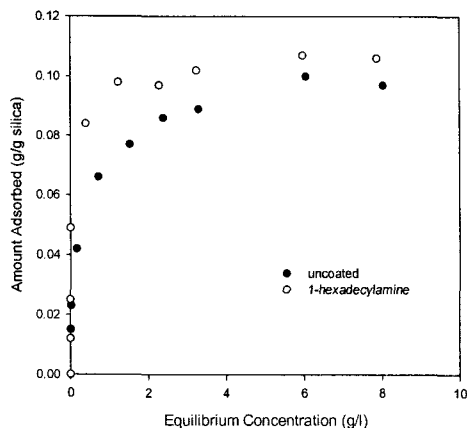Fig. 5. Adsorption isotherms of benzophenone on uncoated and HDTMA silica.

Fig. 6. Adsorption of benzoic acid on uncoated and 1-hex-adecylamine silica.
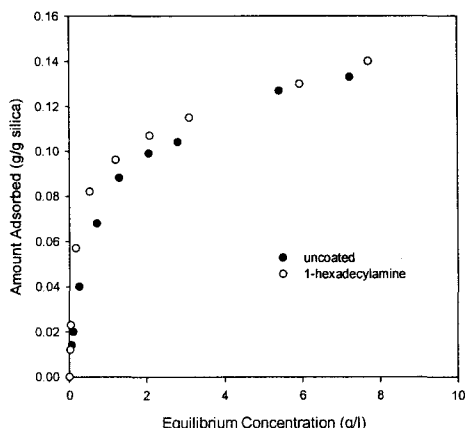

Fig. 7. Adsorption of phenol on uncoated and 1-hexadecyl-amine silica.

in the adsorption of the acidic compounds, benzoic acid and phenol, onto the precoated silica with 1-hexadecylamine. Benzoic acid and phenol can also be adsorbed onto the silanol groups of the silica surface unoccupied by the precoated 1-hexadecylamine through hydrogen bonding. A proposed mechanism for this acid-base interaction is presented in Fig. 8[16].

Quarternary ammonium halides, such as HDTMA, cannot act as Lewis bases because they do not have unshared electron pairs. Thus, acid-base interaction will not occur between the acidic molecules and the HDTMA. This factor can explain the decrease in the adsorption of acidic compounds (benzoic acid and

phenol) onto the precoated silica with HDTMA.

3.3. Adsorption of Acidic Model Compounds on Uncoated Silica and Precoated Silica with 1-hexadecylamine and HDTMA in aqueous environments

Adsorption of the acidic compounds (benzoic acid and phenol) onto the uncoated silica in distilled water solution was compared to those onto the silica pre-coated with 1-hexadecylamine and HDTMA. As shown in Fig. 9, benzoic acid adsorbed more to the precoated silica than to the uncoated silica regardless of the ASAs. As can be seen in Fig. 1 and Fig. 9, adsorption of benzoic acid was reduced substantially when ad-
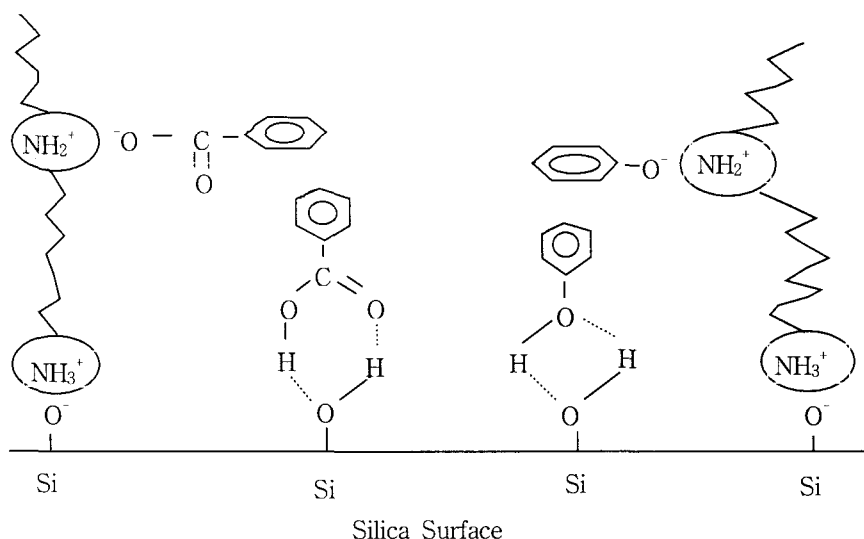

Fig. 8. Acid-base interaction between acidic functionalities and amino groups of polyamine and hydrogen bonding between acidic molecules and silanol groups of silica surface.

sorbed in water solution. Polar water molecules can interact with silanol groups of the silica surface through hydrogen bonding. Therefore, competition existed between benzoic acid and water for the adsorption sites on the silica surface. However, excess water molecules can predominantly occupy the adsorption sites, saturating the silica surface and leaving few active adsorption sites available for benzoic acid. In addition, benzoic acid can dissociate in aqueous solution. The pKa of benzoic acid in water solution at 25℃ is 4.21. Thus, a small portion of benzoic acid can dissociate to form hydronium ions by donating protons to water molecules. Even though the degree of dissociation is not significant, the dissociated benzoic acid become negatively charged. As a result, electrostatic repulsion can develop between the negatively charged benzoic acid and silica surface. These factors can explain the decrease of benzoic acid in water solution.

Benzoic acid adsorbed more to the precoated silica with 1-hexadecylamine than to the uncoated silica in aqueous solution. As the precoating amount of 1-hexadecylamine increased, the adsorption amount of benzoic acid increased. This can be ascribed to the fact that there existed acid-base interaction between benzoic acid and 1-hexadecylamine. As described above, this acid-base interaction may lead to high affinity for the amine-precoated silica, enhancing the adsorption of benzoic acid even in aqueous environments.

Unlike the results in cyclohexane solution as seen in Fig. 1, adsorption of benzoic acid was greater onto the precoated silica with HDTMA than to the uncoated silica in aqueous solution. This can be explained by the fact that precoating of the silica by or-

ganic compound such as HDTMA may make the hydrophilic silica surface become partially hydrophobic, allowing organic molecules to be more adsorbed to the silica surface in an aqueous environment.

As shown in Fig. 10, phenol showed similar adsorption behaviour to that of benzoic acid. Adsorption of phenol onto the precoated silica was greater than that onto the uncoated silica irrespective of ASA. The adsorption behaviour of phenol in aqueous environments can be ascribed to the same factors as described to those of benzoic acid except for the fact that the pKa value of phenol in water at 25℃ is 10 and thus, dissociation of phenol in water can be ignored. Therefore, decrease of phenol in aqueous solution may be considered to be due to the predominant occupation of polar water molecules on the adsorption sites of the silica surface.

4. Conclusions

Adsorption of asphalt model functionalities was affected by the precoating of the silica with HDTMA and 1-hexadecylamine. In cyclohexane solutions, adsorption of all the model functionalities decreased with the silica precoated with HDTMA. Adsorption of the acidic model compounds, benzoic acid and phenol, increased with the silica precoated with 1-hexadecylamine. All the model compounds showed Langmuir adsorption isotherm behaviour.

Adsorption of acidic compounds, benzoic acid and phenol, decreased substantially in water solution because of predominant occupation of excess polar water molecules on the silica surface through hydrogen bonding. However, precoating of the silica with
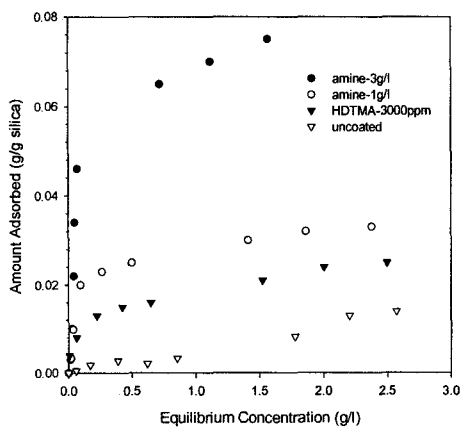

Fig. 9. Adsorption of benzoic acid in aqueous solution.
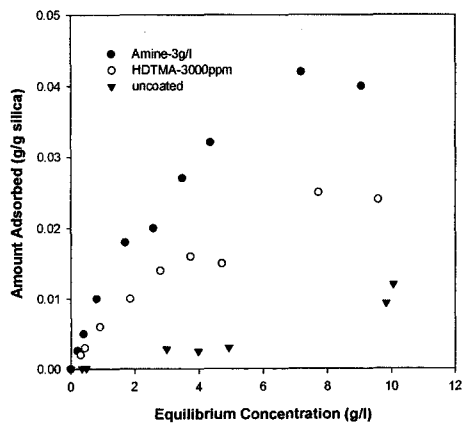

Fig. 10. Adsorption of phenol in aqueous solution.

1-hexadecylamine enhanced the adsorption of the acidic compounds in aqueous solution.

From the results of this study, it is suggested that pretreatment of the aggregate surface with polyamine surfactant such as 1-hexadecylamine increases the adsorption affinities for the aggregate surface and thus, enhances the durability of the asphalt concrete mixtures.

Acknowledgement

References

1) Fromm, H. J., 1974, The mechanism of asphalt stripping from aggregate surface, Proc. Assoc. of Asphalt Paving Technologists, 43, 191-219.

2) Scott, J. A. N., 1978, Adhesion and disbonding of asphalt used in highway construction and maintenance, Proc. AAPT, 47, 19-48.

3) Krutz, N. C. and N. Stroup, 1990, Relationship between permanent deformation of asphalt concrete and moisture sensitivity, Transportation Research Record, 1259, 169-177.

4) Shatawi, S. R. and J. V. Kirk, 1993, Premature asphalt concrete pavement distress caused by moisture induced damage, Transportation Research Record, 1417, 168-177.

5) Jo, M. C., A. R. Tarrer, Y. W. Jeon, S. J. Park, and H. H. Yoon, 1997, Investigation of the effect of aggregate pretreatment with antistripping agents on the asphalt-aggregate bond, Petroleum Science and Technology, 15, 245-271.

6) Jo, M. C. and S. J. Park, 2005, Investigation of the adsorption of asphalt functionalities on silica pretreated with amine-type surfactant, J. Ind. Eng. Chem., 11, 267-274.

7) Mathews, D. H., 1962, Surface-active agents in bituminous road materials, J. of Appl. Chem., 12, 56-64.

8) Anderson, D. A., E. L. Dukatz, and J. C. Peterson, 1982, The effect of antistrip additives on the properties of asphalt cement, Asphalt Paving Technol, 51, 298-317.

9) Coplantz, J. S., J. A. Epps and L. Quilici., 1987, Antistrip additives: Background for a field performance study, Transportation Research Record, 1115, 1-11.

10) Dybalski, J. N., 1982, Cationic surfactants in asphalt adhesion, Proc. Assoc. of Asphalt Paving Technologists, 51, 293-307.

11) Plancher, H., S. M. Dorrence and J. C. Peterson, 1977, Identification of chemical types in asphalt strongly adsorbed at the asphalt-aggregate interface and their relative displacement by water, Proc. AAPT, 46, 151-175.

12) Curtis, C. W., Y. W. Jeon and D. J. Clapp, 1989, Adsorption of asphalt functionalities and oxidized asphalts on aggregate surfaces, Fuel Science and Technology International, 7, 1225- 1268.

13) Jeon, Y. W., C. W. Curtis, and B. M. Kiggundu, 1990, An investigation of the effect of antistripping agents on silica adsorption of asphalt functionalities, Fuel Science and Technology International, 8, 241-270.

14) Park, S. K., M. C. Jo, and J. B. Park, 2000, Adsorption and thermal desorption behavior of asphalt-like functionalities on silica, Adsorption Science & Technology, 18, 675-684.

15) Peterson, J. C., 1986, Quantitative functional group analysis of asphalt using differential infrared spectrometry and selective chemical reactions, Transportation Research Record, 1096, 1-11.

16) Jeon, Y. W., 1991, Single- and multi-component adsorption of asphalt functionalities and fractions onto aggregate surfaces, Dissertation, Auburn University, U.S.A., 75.