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QUANTITATIVE STRUCTURE–PROPERTY RELATIONSHIPS OF ANTIWEAR PERFORMANCE OF LUBRICANT ADDITIVES

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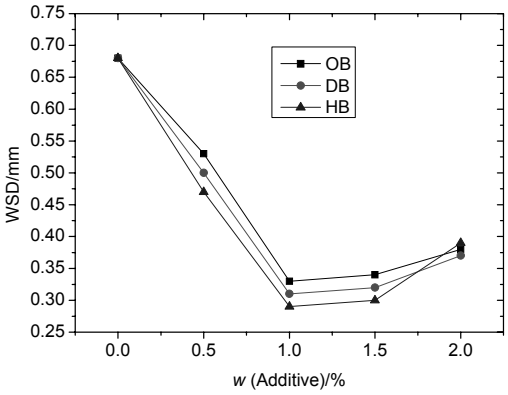
A multiple linear regression (MLR) model based on 35 lubricant additives was developed to predict antiwear performance. Compared with existing models, the three-descriptor MLR model with a squared correlation coefficient R^2 of 0.859 is accurate and acceptable. By means of the prediction results from MLR model, three new lubricant additives containing benzimidazole and xanthate groups (O-octyl- S-benzimidazolylmethyl xanthate, OB; O-dodecyl-S-benzimidazolylmethyl xanthate, DB; and O-hexadecyl- S-benzimidazolylmethyl xanthate, HB) are designed and synthesized. Their experimental results of antiwear ability measured by wear volume (*WV*) (i.e., 4.10 for OB, 4.18 for DB and 4.26 for HB) are in accordance with the theoretical predictions (4.22, 4.26 and 4.27, respectively). Thus, applying QSPR models to design and synthesize lubricant additives is feasible.



INTRODUCTION

Friction process of machines consumes a lot of energy, accounting for 1/3 of primary energy consumption.[1] For example, in China, the economic loss resulted from friction and wear in 2006 was up to 950 billion yuan. While by applying tribological achievements, at least 327 billion yuan may be saved.[2] Lubrication is an effective method to reduce friction and wear. Lubricating oil additives can improve the performance of lubricants. Nitrogen-containing heterocycle derivatives as multifunctional lubricating oil additives have exhibited good extreme pressure and antiwear properties. A lot of work has focused on the preparation and performance test of lubricant additives.

Many researchers have recognized the importance of carrying out studies on the chemical structure of lubricant additives. Among these works, the relationships between chemical structure and lubrication mechanism were interpreted only qualitatively.[3, 4] Hu and Liu reported the tribological properties of a series of alcohols as lubricating additives in liquid paraffin and found that the load-carrying capacity and antiwear ability of these compounds increased with the increase of hydroxyl group number in the alcohols.[5] Tan et al. illustrated the interaction between lubricant additives and metal surfaces and clarified the lubricating mechanisms by applying molecular orbital calculations.[6,7] Wang et al.

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adopted density functional theory to study structure-property relationships for phosphorus additives, disulfide compounds, and alkylated arylamines as lubricant additives.[8-10]

Though antiwear mechanism has not been fully understood, molecular quantitative structure-properties/activity (QSPR/QSAR) of lubrication additives can reveal the relationships between molecular structures and tribological properties and find the structure factors that affect tribological properties. Thus, QSPRs of lubrication additives can be used to screen any number of compounds, including those not yet synthesized, and to select some compounds with the desired structures and properties.[11] However, as we know, there are only a few QSPR models reported on lubrication additives. The reasons may be that experimental errors in tribological performance test for lubricating oil additives are relative large and experimental data for lubricating oil additives are insufficient, which lead to it difficult to carry out QSPR studies for lubricating oil additives.

Cholakov et al. introduced a model that could predict the tribological property of organic sulphides. This model was based on tribochemical kinetics and developed through molecular design with principle components.[12] Gao's team developed quantitative structure tribo-ability relationship (QSTR) model for lubricant additives of N-containing heterocyclic derivatives with multiple linear regression (MLR) analysis.[13, 14] The model based on 17 lubricant additives and two quantum chemistry descriptors, *i.e.*, the total energy and dipole, has correlation coefficient R of 0.94;[12] the models based on 36 lubricant additives and the same quantum chemistry descriptors give correlation coefficients of 0.526, 0.622, and 0.561 for wear-scar area data obtained under three loads: 196 N, 294 N and 392 N.[14] Gao's team further presented QSTR models for the same dada set of 36 heterocyclic additives with a back propagation neural network (BPNN).[15] The QSTR models have subsets of 47 or 60 molecular descriptors. According to Reference[16], an acceptable QSAR model should have a higher R value ($R^2 > 0.5$) and a large ratio ($n/N > 5$) of the number of samples (n) to the number of descriptors used (N). The research suggests that the models[14,15] should be improved.

To design and synthesize lubricating additives would be of great importance for decreasing energy consumption. The aim of this paper is to develop a QSTR model under high load of 392 N for lubricant additives of N-containing heterocyclic derivatives, from which three new lubricant oil additives with good antiwear ability are designed, synthesized and tested.

MATERIAL AND METHODS

Figure 1 shows the structures of five matrices of N-containing heterocyclic derivative: benzoxazole, benzimidazole, benzothiazole, thiazoline and piperazine. Table 1 lists 36 molecular structures based on above five matrices. Table 2 shows their respective tribological data obtained with a four-ball machine and tested under the experimental conditions of Chinese national standard GB3142-82, similar to ASTM D-2783. As such, a velocity of 24.17 r/s is applied for 30 min at room temperature. The GCr15 balls used for the experiments have a diameter of 12.7 mm. The balls are hardened to 59–61 HRC.[17] The wear scar diameters (*WSD*) were measured under the load of 392 N. Wear volumes (*WV*) are used to describe molecule lubricity at the optimal concentration with the following expression:

$$WV = \log_{10} \frac{(WSD_0^{3/2} - WSD^{3/2}) \cdot MW}{Conc} \qquad (1)$$

Where WSD_0 is the wear-scar diameter (mm) formed under pure base paraffin oil; *WSD* is the wear-scar diameter (mm) formed using the lubricant additives; *MW* is the molecular weight of lubricant additives; and *Conc* is the concentration (weight percent, wt%) of lubricant additives to obtain the best lubrication.[15, 17] A large value of *WV* denotes the corresponding additive has good antiwear performance.

The lubricant additives in Table 2 were divided into a training set (24) and a test set (12). The training set was used to develop models and the test set was used to validate the models.

ChemBioDraw Ultra 11.0 in ChemOffice 2008 was used to sketch the molecular 2D structures, which were then converted to 3D structures and optimized using a molecular mechanics (MM2 force field) in ChemBio3D Ultra 11.0 with the convergence criterion of minimum root-mean-square (*RMS*) error of gradient value being 0.01 kcal/molÅ. Lastly, Dragon 6.0 software[18] was used to calculate 4885 descriptors for each energy-minimized molecule. In order to reduce redundant and non-useful information, descriptors being constant or near constant were removed. Similarly, descriptors with pair correlation greater than or equal to 0.90 were also deleted. After excluding redundant and non-useful descriptors, 442 variables remained to undergo descriptor selection.

A relative optimal subset of descriptors used for QSPR models was obtained by applying MLR analysis. MLR is the most commonly used statistical method in selecting the best descriptor subset and develop MLR model.

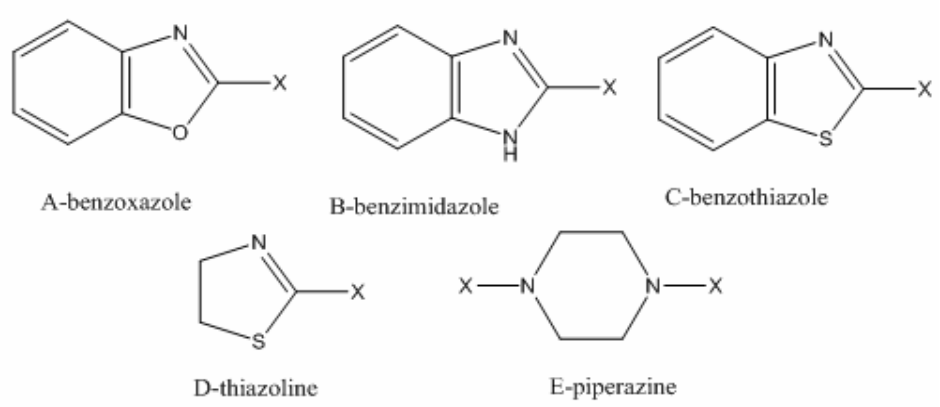

Fig. 1 – Structures of matrices of lubricant additives.

Table 1

Molecular structures of 36 lubricant additives

No.	Matrices	Substituent X	No.	Matrices	Substituent X
1	A	$S_2C_{12}H_{25}$	19	C	$SCH_2CH(OH)CH_2SP=S(OC_{12}H_{25})_2$
2	A	$S_2C_8H_{17}$	20	A	$SCH_2N(C_4H9)_2$
3	A	$S_2C_4H_9$	21	A	$SCH_2N(C_8H_{17})_2$
4	B	$S_2C_{12}H_{25}$	22	B	$SCH_2N(C_4H_9)_2$
5	B	$S_2C_8H_{17}$	23	B	$SCH_2N(C_8H_{17})_2$
6	B	S2C4H9	24	C	$SCH_2N(C_4H_9)_2$
7	C	$S_2C_{12}H_{25}$	25	C	$SCH_2N(C_8H_{17})_2$
8	C	$S_2C_8H_{17}$	26	D	$SCH_2N(C_4H_9)_2$
9	C	$S_2C_4H_9$	27	D	$SCH_2N(C_8H_{17})_2$
10	C	$SCH_2CH(OH)CH_2SC=S(OC_2H_5)$	28	C	SC_3H_7
11	C	$SCH_2CH(OH)CH_2SC=S(OC_4H_9)$	29	C	SC_8H_{17}
12	C	$SCH_2CH(OH)CH_2SC=S(OC_5H_{11})$	30	C	SC_3H_5
13	C	$SCH_2CH(OH)CH_2SC=S(OC_8H_{17})$	31	B	SC_3H_7
14	C	$SCH_2CH(OH)CH_2SC=S\ [\ N(C_2H_5)_2\ ]$	32	B	SC_3H_5
15	C	$SCH_2CH(OH)CH_2SC=S\ [\ N(C_4H_9)_2\ ]$	33	A	SC_3H_5
16	C	$SCH_2CH(OH)\ CH_2SC=S\ [\ N(C_8H_{17})_2\ ]$	34	E	$S=CSC_{10}H_{21}$
17	C	$SCH_2CH(OH)CH_2SP=S(OC_4H_9)_2$	35	E	$S=CSC_8H_{17}$
18	C	$SCH_2CH(OH)CH_2SP=S(OC_8H_{17})_2$	36	E	$S=CSC_4H_9$

Table 2

Wear volume and descriptor values of lubricant additives

Derivative number	*NP*	*GATS1s*	*R3m*	*VS*(exp.)	*VS*(MLR)
Training set					
1	0	0.803	0.030	4.34	4.27
2	0	0.796	0.036	4.63	4.25
4	0	0.902	0.031	4.18	4.12
5	0	0.895	0.034	4.08	4.12
7	0	0.837	0.086	3.96	3.93
8	0	0.820	0.095	3.75	3.90
10	0	0.949	0.091	4.07	3.74
11	0	0.925	0.063	4.05	3.92
13	0	0.900	0.056	3.92	3.99
9	0	0.831	0.083	3.20	/
16	0	0.886	0.083	3.82	3.87

Table 2 (continued)

17	1	1.053	0.076	5.18	5.00
19	1	1.019	0.039	5.07	5.25
20	0	0.879	0.045	4.02	4.08
22	0	0.994	0.040	3.95	3.94
23	0	1.003	0.023	4.00	4.02
25	0	0.960	0.041	3.79	3.98
26	0	1.032	0.059	3.72	3.78
28	0	0.858	0.070	3.95	3.98
29	0	0.840	0.060	4.10	4.06
31	0	0.948	0.089	3.45	3.75
32	0	1.110	0.079	3.63	3.57
34	0	0.689	0.037	4.35	4.40
35	0	0.666	0.042	4.32	4.41
Test set					
3	0	0.818	0.045	4.47	4.17
6	0	0.919	0.041	3.96	4.04
14	0	0.930	0.093	3.31	3.75
12	0	0.917	0.060	4.09	3.95
15	0	0.903	0.089	3.50	3.81
18	1	1.026	0.046	4.96	5.20
21	0	0.891	0.039	4.05	4.10
24	0	0.938	0.042	3.65	4.01
27	0	1.077	0.051	3.51	3.76
30	0	1.056	0.081	4.03	3.63
33	0	1.006	0.084	3.76	3.69
36	0	0.624	0.056	4.60	4.40
Designed molecules					
OB	0	0.747	0.055	4.10	4.22
DB	0	0.747	0.047	4.18	4.26
HB	0	0.754	0.044	4.26	4.27

RESULTS AND DISCUSSION

QSPR and molecular design

By analyzing the correlation between the 442 descriptors and *WV* of 24 lubricant additives in the training set with stepwise MLR analysis in IBM SPSS Statistics 19, Eq. 2 and the corresponding statistical results were obtained.

$$WV = 5.455 + 1.335\,NP - 1.209\,GATS1s - 7.005\,R3m \quad (2)$$
$$R=0.880,\ R^2=0.774,\ SE=0.226,\ F=22.877,\ N=24$$

where R is the correlation coefficient; N is the number of samples from the training set; SE is the standard error of estimate; F is the Fischer ratio. Three molecular descriptors, i.e., *NP*, *GATS1s* and *R3m*, appear in above MLR model. *NP*, belonging to constitutional indices, denotes the number of phosphorous atoms. GATS1s is Geary autocorrelation of lag 1 weighted by I-state. *R3m* represents *R* autocorrelation of lag 3 / weighted by mass. These descriptor values are shown in Table 2.

By Eq. 2, the sample, Benzothiazole with a substituent $-S_2C_4H_9$ (No. 9 in Table 1), has an experimental *WV* value of 3.20, a calculation *WV*

value of 3.86, and a standardized residual (ZRE) of 2.91. According to statistical theory, if a sample possesses a larger ZRE, e.g. ZRE ≥ 3, it should be considered to be an outlier. Therefore, we deleted this sample from the training set, and rebuilt Eq. 3. The calculation results are shown in Table 2; and statistical characteristic values of descriptors are shown in Table 3.

$$WV = 5.599 + 1.338\,NP - 1.457\,GATS1s - 5.268\,R3m \quad (3)$$
$$R=0.927,\ R^2=0.859,\ SE=0.167,\ F=38.663,\ N=23$$

Table 3

Characteristics of descriptors in Eq. 3

Descriptor	**Coefficients**	***SE***	***t***	***Sig.***	***VIF***
Constant	5.599	0.317	17.644	0.000	/
NP	1.338	0.134	9.975	0.000	1.178
GATS1s	-1.457	0.359	-4.056	0.001	1.218
R3m	-5.268	1.595	-3.302	0.004	1.038

Table 3 shows that all the *Sig.* values of the three descriptors are less than 0.05, which indicate that these descriptors are significant ones. The *VIF* value for each descriptor is less than the default value of 10, which shows that these descriptors are weakly correlated with each other.

According to the *t*-test, the most significant descriptor in Eq. 3 is *NP*. A molecule has more phosphorus atoms, the lubricant additive has better antiwear and lubricity ability, which decreases wear-scar area. Thus the lubricant additive possesses a higher *WV* value. It has been tested that the reactive phosphor element in a lubricant additive can result in tribo-chemical reaction on the metal surface and generate a chemisorbed film with high compressive strength, low shear strength and melting point, which prevents direct contact of metal friction pairs and improves tribological properties.[19]

By the *t*-test, the second significant descriptor in Eq. 3 is the 2D correlation parameter *GATS1s*. This descriptor is related to the molecular size and symmetry. While molecular structural factors, such as molecular size and polarity, affect their surface adsorption and film-forming property. The last significant descriptor is the GETAWAY (GEometry, Topology, and Atom-Weights AssemblY) descriptor *R1m*. GETAWAY descriptors are based on spatial autocorrelation, encode information on structural fragments and information on the effective position of substituents and fragments in the molecular space. Therefore, GETAWAY descriptors seem to be particularly suitable for describing differences in congeneric series of molecules. The descriptor *R1m* accounts the 3D molecular structure information on molecular size and shape as well as for specific atomic properties, which may be related to additive's property of surface adsorption and chemical reaction.

The MLR model from the training set in this paper has a squared correlation coefficients R^2 of 0.859 and *RMS* error of 0.151; for the test set, R^2 = 0.689, *RMS* = 0.268. The entire data set, R^2 = 0.789, *RMS* = 0.199. The statistical results are superior to those from Reference[14] with *R* = 0.561, *RMS* = 0.38791 (under the load of 392 N). In this paper, the squared correlation coefficients R^2 of the MLR model obtained is greater than the default criterion of 0.5.[16, 20] Moreover, in this paper, the ratio (23/3 ≈ 7.7) of the number of samples (23) to the number of variables (3) is greater than 5. Therefore, the MLR model in this paper has statistical significance. Compared to models,[14, 15] our MRL model is accurate and acceptable.

From the point of view of environmental protection, derivatives of xanthic acid as ashless and extreme pressure antiwear additive have a good application prospect.[21] Therefore, based on our MLR model, we designed three N-containing heterocyclic lubricating additives based on benzimidazole (the matrix structure B in Fig. 1): O-octyl-S-benzimidazolylmethyl xanthate, OB (Substituent X being $CH_2SC{=}S(O\text{-}C_8H_{17})$); O-dodecyl-S-benzimidazolylmethyl xanthate, DB (Substituent X being $CH_2SC{=}S(OC_{12}H_{25})$); and O-hexadecyl-S-benzimidazolylmethyl xanthate, HB (Substituent X being $CH_2SC{=}S(OC_{16}H_{33})$). Three descriptors (*NP*, *GATS1s* and *R3m*) of BO, BD and BH were calculated and listed in Table 2. According to Eq. 3, their *WV* values are 4.22, 4.26 and 4.27, respectively. These prediction values are greater than the average *WV* value (4.03) of 36 additives in Table 2. This means that the new designed additives (OB, DB and HB) should have good antiwear performance.

Additive synthesis and evaluation

Figure 2 is the synthetic routes of new additives, OB, DB and HB. Three steps were adopted. The first step is to synthesize O-octyl (or O-dodecyl, or O-hexadecyl) sodium xanthate; the second step is to synthesize (chloromethylene)-benzimidazole; and the third step is to synthesize target additives. The specific experimental conditions can be found in Reference.[22]

The tribological behaviors of the three synthesized compounds as the additive in liquid paraffin were investigated by using a four-ball machine. Chinese national standard GB3142-82 similar to ASTM D-2783 is used for the tests. Figure 3 shows the relationships between additive concentration and *WSD*, under the load of 392 N. As can be seen, the new additives, OB, DB and HB, could improve the antiwear ability of liquid paraffin. Moreover, for each new additive, the maximum antiwear ability occurs at an additive mass fraction of 1.0 %. Thus, the relative optimal additive concentration for each additive OB, DB or HB is set as 1.0 %.

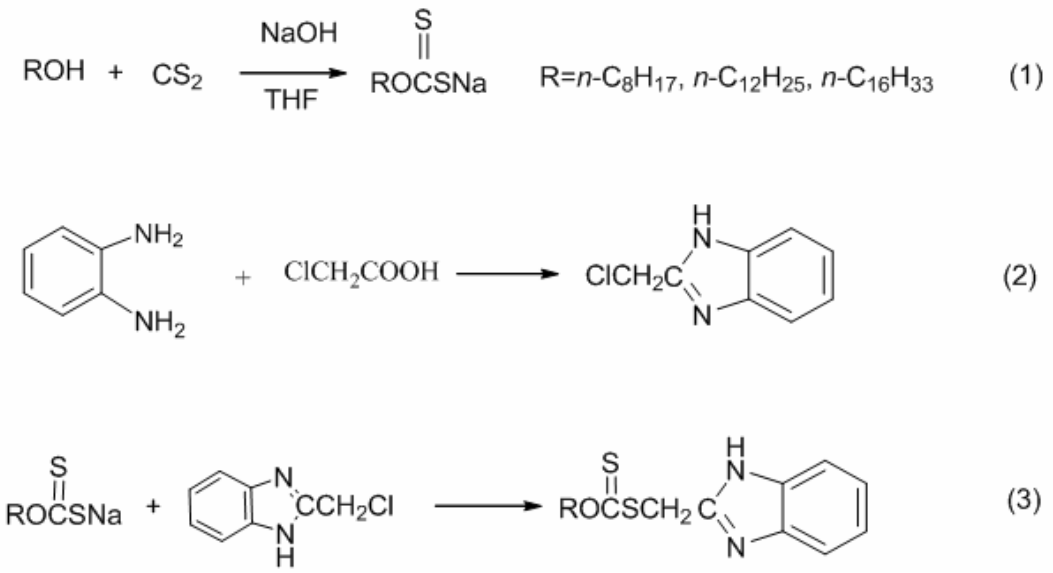

Fig. 2 – The synthetic routes of compounds.

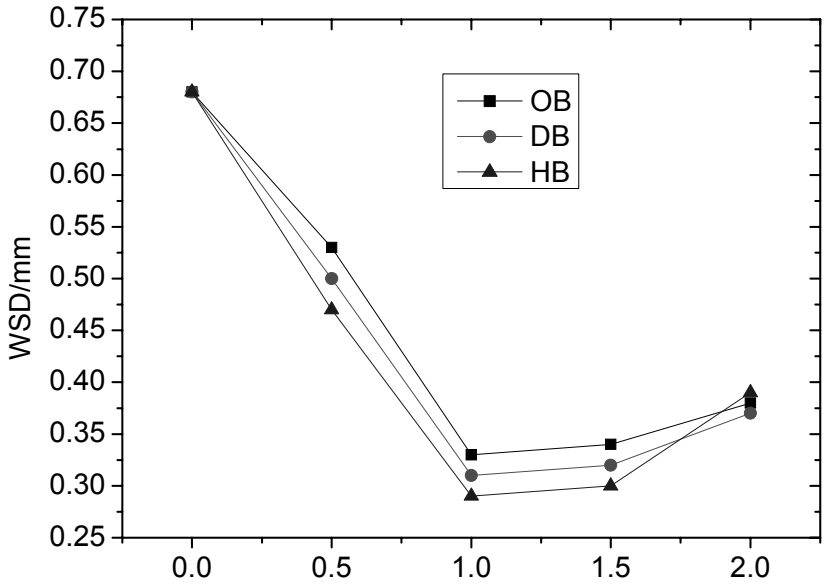

Fig. 3 – Relationship between additive concentration and *WSD*.

By measuring antiwear properties of base oils without additives, the *WSD* value of 0.68 mm was obtained; when the new additives (with mass fraction of 1.0 %) were added for based oil, the *WSD* values obtained are 0.33 mm for OB, 0.31 mm for DB and 0.29 mm for HB. Their molecular weights are 336.57, 392.69 and 448.81, respectively. According to Eq. 1, the experimental *WV* values are 4.10 for OB, 4.18 for DB and 4.26 for HB, which are in accordance with the theoretical values (4.22, 4.26 and 4.27, respectively). Therefore, by applying QSPR models, designing and synthesizing lubricant additives is feasible.

CONCLUSIONS

By means of MLR technique, a QSPR model of 35 lubricating additives was constructed to predict the antiwear properties characterized with *WV*, under the load of 392 N. Three molecular descriptors were used as characteristic variables to develop the model, which has squared correlation coefficients R^2 of 0.859 for the training set (23 lubricating additives), 0.689 for the test set (12 lubricating additives), and 0.789 for the total data set (*RMS* = 0.199). Compared to existing models, the model proposed is successful and possesses statistical significance. Based on the model prediction results, three lubricating additives were designed, synthesized and tested. The experimental results are in accordance with the theory predictions from our MLR model. The investigation demonstrates the powerful ability of QSPR aided molecular design of lubricant additives.

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