Influence of acid-base and adsorptive characteristics of disperse aluminum modified by ammonium compounds on antifriction effect in lubricant

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Abstract. The article analyses the acid-base and adsorptive characteristics of the metal samples obtained using method of layering of different-sized molecules of quaternary ammonium compounds (QAC). The method allows to vary the hydrophilic-lipophilic, antifriction and other properties of commonly used disperse metals. The method includes the process of adsorption of reagents such as QAC based triamon (C_1-C_2) and alkamon (C_{16}-C_{18}), which have very different in length hydrocarbon radical at nitrogen atom. The acid-base properties of modified disperse aluminum were studied using Hammett indicator method and it has been established that there is a change in the quantity of the donor-acceptor centers of the powder caused by the adsorption of QAC. Spectrophotometric analysis of surface centers was performed using the Hammett indicators within the range of pKa values from -0.3 to 14.2. The distribution curves of the active adsorption centers of aluminum-based powders were plotted against the acid dissociation constant (acid strength - pK_a) of the indicators. A sharp decrease is observed in the number of centers in the Lewis acid sites region for the Al/(A+T) sample with co-adsorbed alkamone (A) and triamon (T). In addition, significant decrease in antifriction and water-repellent properties of the sample Al/T/A (consistent treatment of metal in vapor of T and A) in comparison with sample Al/(A+T) is explained by the increase of Bronsted base centers with pK_a = 9.5 and less intense interaction of QAC with Lewis acid centers with pK_a = 14.2.The following pattern was revealed: increase in the antifriction effect of oil based lubricants is accompanied by reduction of the Bronsted centers content and as a rule by the decrease of acidity function (H) of the surface of the QAC-modified Al-powder which was added to the lubricant.

1. Introduction

According to modern views,based on the classical works of Tanabe, the surface of solids consists of Lewis and Bronsted acid and base centers [1 - 4]. The spectrum of the distribution of adsorption centers (DAC) allows to predict the reactivity and sorptive characteristics of the surface and other physico-chemical properties of solids used as catalysts, fillers of composite and nanostructured materials [2, 4].

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Using the method of adsorption of Hammett acid-base indicators [1], it is possible to determine the content of active centers, their distribution in terms of the ionization constant and the value of the Hammett acidity function. Previously conducted experimental research was mainly dedicated to the study of surface of solid oxides [1-3]. However, conducted scientific works have not sufficiently studied the stabilized disperse metals, such as aluminum powder, containing on the surface different-dimensional molecules of ammonium compounds, which possess electron-donating properties [5, 6]. At the same time, mentioned information is extremely important for studying the adsorption of modifiers on the surface of disperse metals, used as additives to the oil lubricant [7, 8].

The main goal of this work is to study the change in the acid-base properties of the surface of disperse aluminum caused by the adsorption of quaternary ammonium compounds, and to find corresponance of these properties with the antifriction effect of modified powders as additives to the oil lubricant.

2. Materials and methods

We have studied the distribution of donor-acceptor centers along the surface of the original aluminum powder (PAP-2, specific surface area = 2.6 m^2/g) and powder modified by various adsorption mechanisms in vapors of quaternary ammonium compounds (QAC). Mentioned methods of layering of QAC on metals (Al, Cu, Ni) from gas phase are fully described in the literature [5-8]. QAC-based surfactants were used as adsorbates: alkamon (A) and triamon (T). Composition of triamon corresponds to the chemical formula $[(HOC_2H_4)_3N^+CH_3][CH_3SO_3^-]$tris-(β-oxyethyl) methyl- ammonium-methyl sulfate; adsorbate A has a similar composition, but with a higher-molecular-weight radical (C_{16}-C_{18}) at the nitrogen atom [9]. The following types of samples have been obtained: with adsorbed T (Al/T), with adsorbed A (Al/A) and the sample with adsorbed A and T in mixture (Al/(A+T)). Powder Al/(A+T)previously has shown better hydrophobic and antifriction properties [5, 10, 11].

The measurement of the number of active center (q) was performed by spectrophotometric indicator method [3, 12] using acid-base indicators with pK_a value within the range from -0.3 to 14.2 and device PE5400UF. The indicators are listed with their values of ionization constants: Orthonitroaniline (-0.3), Brilliant green (1.5), Fuchsine (2.1), Xylenol orange (2.6), Methyl orange (3.5), Bromophenol blue (4.1), Methyl red (5.0), Bromocresol purple (6.4), Phenol red (8.0), Phenolphthalein (9.5), Alizarine Yellow (11), Indigo carmine (12.8), Thymolphthalein (14.2).

The methods of measuring solution density and calculation of the change in the optical density (ΔD) after adsorption of the indicators and the number of surface centers of a given strength (q_{pKa}) are described in the works [3, 12, 13]. The Hammett acidity function was calculated from equation: $H_0 = \sum pK_a \cdot q_{pKa} \Big/ \sum q_{pKa}$ .Root mean square error of independent measurements of the optical density of one sample is $\Delta q_{pKa} = \pm 0.40\%$.

3. Results and discussion

Surface of the Al-based samples can be characterized as a set of Lewis and Bronsted acid and base centers (figure 1) which are able to interact with Hammett indicators.

The obtained experimental data shows that interaction of indicator and Al surface leads to the adsorption of certain indicator on the active centers with only corresponding acid strength. The adsorption of indicators provides changes in coloration of the solution, which can be observed spectrophotometrically. Such method is used to characterize the amount of certain active centers.

Indicators with lower dissociation constant are selectively adsorbed on the Lewis base centers. With the increase of acid strength of indicators, they are adsorbed on Bronsted acid ($0 < pK_a < 7$) and base ($7 < pK_a < 14$) centers. At the value of $pK_a > 14$ the adsorption occurs on the Lewis acid centers [3, 12].

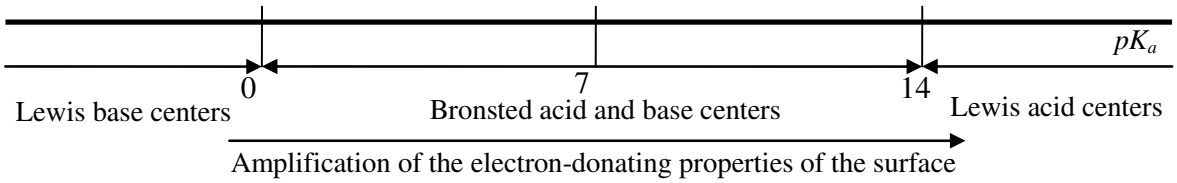


Figure 1. Formal layout of acid-base surface centers in respect to strength and type (typical for partially dehydrated amphoteric oxides, such as aluminum oxide).

Surface layer of the initial Al-powder PAP-2 consists of aluminum and aluminum oxide structures. This fact is proved by the following X-ray photoelectron spectrum peaks: for aluminum which appears at lower binding energies ($E_{binding}$ = 72.4eV – Al2p), for oxidized aluminum ($E_{binding}$ = 74.6eV – Al2p) and for oxygen ($E_{binding}$ = 531,3 eV – O1s), which is presented in the aluminum oxide structures [5]. Industrially manufactured powder PAP-2 contains stability agent – non-unifirm stearine nanofilm [14]. The thickness of Al-oxide layer may reach 0,002 μm [7, 14]. According to the research [15], stearine has low adsorption activity which is proved by the little adsorption (approximately 0,03 μmol/g) of Hammett indicators on the stearine in the experiments [7].

According to the characteristics of the DAC-spectrums (figure 2), all samples have 4 types of peaks on distribution curves: pK_a= -0.3; 5; 9.5; 14.2. Initial Al-powder contains mostly Lewis acid centers (pK_a= 14,2), which correspond to the centers with vacant atomic orbital at Al atom and capable to take an electron pair [2, 12]. Additionally, the composition surface of initial metal includes Bronsted base centers (pK_a= 9,5) which correspond to OH-groups. The peaks corresponding to Bronsted acid and base centers (pK_a= 5 and pK_a= 9,5) indicate the existence of hydrate-hydroxyl layer on the initial Al-powder surface [16,17]. Therefore, it has been concluded that initial powder is oxidized. In case of application of alkamon or triamon (curves II, III), there is a significant decrease in the number of Lewis acid centers with pK_a 14.2. However, when these substances are applied together from the mixture (A+T), the number of these centers decrease by more than an order of magnitude (curve IV). It is obvious that the adsorption of QAC occurs on Lewis acid centers. Moreover, when vapor mixture (A+T) is used the number of covered acid centers reaches the similar quantity to which could be provided by using vapours of triamon and alkamon separately taken together. This observation correlates with the concentration of QAC in the samples: Al/A – 0,13 mol %, Al/T – 0,22 mol %, Al/(A+T) – 0,32 mol % [6]. The most probable mechanism of adsorption of QAC on aluminum powder is the donor-acceptor interaction of the cation part $[N^+R_1R_2R_3R_4]$ of the adsorbate molecule with electron-accepting centers of the aluminum surface (R_1, R_2, R_3, R_4 – the radicals at the nitrogen atom in the compounds).

Adsorption of QAC occurs on the base OH-groups (pKa= 9,5), however in this case, the application of adsorbate (A+T), as seen from figure 2, does not provide the sum of the covered centers observed when applying A and T separately. The possibility of adsorption of hydrophobic QAC molecules on hydrophilic surface centers caused by the presence of polar groups ($CH_3SO_3^-$) in the structure of these molecules [9, 15].

The mechanism of changes in the peaks amplitude at pK_a= 5 and pK_a= -0,3 is far more complicated. Alkamon and triamon separately are capable to increase the amount of acid centers at pK_a= 5, however, at pK_a= 2,6 and pK_a= -0,3 only alkamon is capable to provide such results. Most probably, the mentioned increase is connected with addition of acid centers of each modifier (A or T) itself to the system. This hypothesis is proved by nearly constant value of specific surface area before and after the modification: (2.6 ± 0.1) m^2/g [5–7].

It is important to note that mixed adsorption of A and T (A+T, mass ratio A:T ≈ 1 [5]) provides significant results in coverage all types of centers listed, as shown in figure 2 (curve IV). The decrease in amount of acid centers was estimated by the change in amplitude of corresponding peaks.

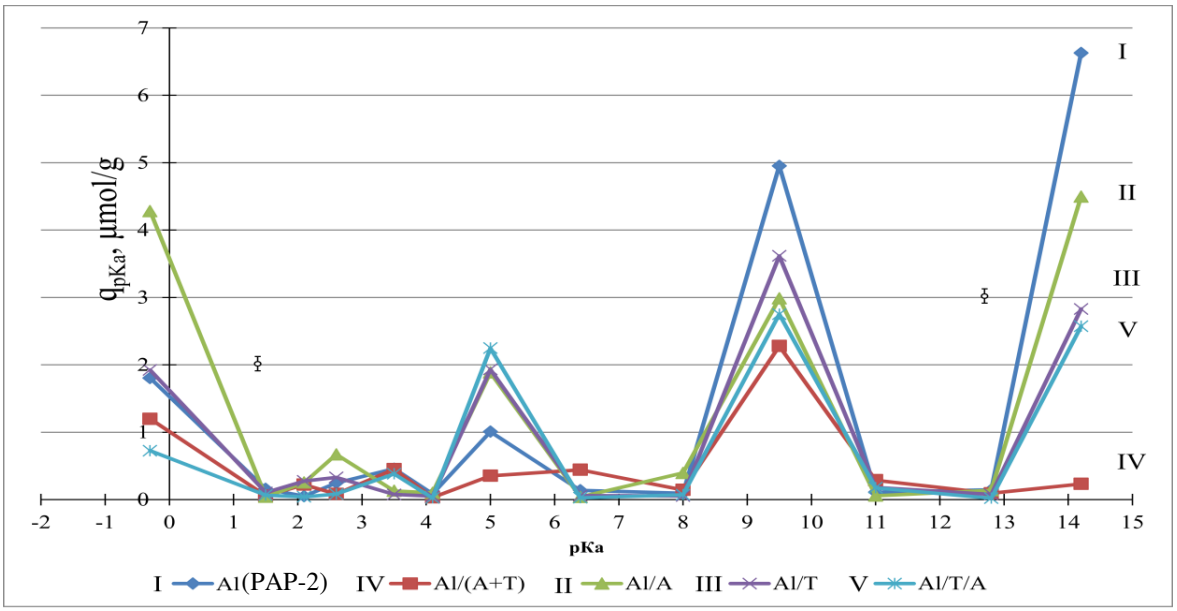


Figure 2. Distribution of acid-base centers on the surface of modified Al-powders.

According to the data presented in figure 2, total number of centers decreases depending on the adsorbate in the row: A, T, A+T. In addition, application of mentioned QAC leads to the decline of the acidity function, as shown in table 1 and according to the row: Al (PAP-2), Al/T/A, Al/T, Al/A, Al/(A+T).

Thus, the acid-base properties of disperse aluminum were studied using Hammett indicator method and it has been established that there is a change in the quantity of the donor-acceptor centers of the powder caused by the adsorption of QAC. The obtained data about the structure of the surface of the samples enables us to broaden the understanding about the evolution of the acid-base properties of the aluminum powder surface during the adsorption of ammonium compounds. These results provide new insights on the previously described [5 - 8, 11] mechanisms of enhancement of the hydrophobic and antifriction properties of the modified powder Al/(A+T), and on the increase of its chemical stability during atmospheric oxidation. The DAC-spectrums confirm that the adsorption of QAC occurs due to the formation of metal-nitrogen heteroatomic interaction with a shift of the electron density from metal to nitrogen, which is detected by X-ray photoelectron spectroscopy [5, 7, 8]. This data does not contradict the views that QAC, due to their diphylic nature, can be adsorbed on different active centers [5], such as Lewis acid and Bronsted basic groups of the surface (see peaks at pK_a 14.2 and 9.5 in figure 2). In addition, there is a trend towards a decrease in the total number of centers and surface acidity during mixed adsorption of A and T, which indicates greater possibility of occurrence of synergistic effects for Al/(A+T) sample rather than for Al/A and/or Al/T samples. These effects have been recorded for various properties and characteristics: hydrophobicity [5], decrease in the integral index, force and friction coefficient in lubricants with additives of Al/(A+T) [8, 11]. According to the table 1 the following trend is observed: the listed tribological characteristics decrease relatively to the acidity function H_0 and the number of active centers with pK_a 9.5 and 14.2 of the disperse additive of modified aluminum which is used in the oil lubricant.

It is interesting for the purpose of the research to compare the properties of Al/T/A (sequential layering of T and A) and Al/(A+T) samples, which contain both modifiers (A and T) and have different nitrogen content of chemisorpted QAC on the surface (0.55 and 0.32 mol% respectively). Interpretation and explanation of the substantially different properties of these samples, especially antifriction is very

complicated [8]. New DAC-spectra analysis allows to relate the mentioned difference to less intense fulfillment of electron-accepting centers of surface (q=2.57 μmol/g – Al/T/A against q=0.24 μmol/g – Al/(T+A) for pKa = 14.2.

Another reason of increase of force of friction in case of Al/T/A sample can be a result of distinct hydrophilization of the surface. Truly, the concentration of hydrophilic centers, which represents the appearance of the hydrate-hydroxyl cover, is greater in case of Al/T/A than in case of Al/(A+T): 2.75 against 2.28 μmol/g for pKa = 9.5.

Table 1. Comparison of the acidity of the surface (H_0) of aluminum-based powders, the number of active centers (q) with different pK_a (9.5 and 14.2) and tribological characteristics of industrial oil I-20 with modified aluminum powder.

Disperse additive to the oil lubricant (1 mass %)	Adsorption of water from saturated vapors by an additive (g/g) [5, 8]	Coefficient of friction [11]	Force of friction, N (P=17 MPa, steel-bronze) [11]	Integral index of friction D (P=51MPa) [5, 7, 8]	q, μмоль/г		H_0
					pK_a14.2	pK_a 9.5	
Al (initial)	0.0023	0.0092	45.06	1690	6.63	4.95	9.65
Al/T	0.0017	0.0077	37.60	780	2.83	3.62	7.77
Al/A	0.0021	0.0076	37.03	910	4.50	2.99	7.06
Al/T/A	0.0016	0.0074	36.50	1000	2.57	2.75	8.54
Al/(A+T)	0.0013	0.0064	31.57	300	0.24	2.28	6.32

One of the possible reasons for the unusual properties of the Al/(A+T) sample in comparison with the Al/A and Al/T samples can be the formation of new adsorptive compound Al/T···A in the surface layer of aluminum due to structural similarity of the T and A molecules, which is accompanied by an experimentally recorded increase in the binding energy of electrons of the characteristic level N1s by approximately 2 eV [5, 7, 10].

4. Conclusion

Under other equal conditions reduction of friction force and coefficient of friction in the studied tribosystem occurs as a rule when the acidity H_0 and the content of the Brensted basic centers of modified aluminum decrease respectively.

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