

# IMPREGNATED FIBROUS CHEMISORBENTS FOR THE COLORIMETRIC DETECTION OF AMMONIA

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The paper presents research results on the colorimetric behavior of impregnated fibrous chemisorbents (IFCS) of basic gases with visual identification of the dynamic absorption capacity “response” moment (IFCS-I) during the absorption of ammonia. Chemisorbents were obtained by impregnation of fibrous carriers with polybasic hydroxyl acid aqueous solutions with adding acid-base indicators (Ind). IFCS-I based on oxyethylenediphosphonic (IFCS-OEDPA-I), citric (IFCS-CA-I), and malic (IFCS-MA-I) acids were used. Azolithine (Az), lakmoid (LA), methyl orange (MO), methyl red (MR), Tropeolin OOO (TrOOO), Congo red (CoR), bromocresol green (BCG), broxylenol blue (BXB), bromophenol blue (BPB), bromophenol red (BPR), thymol blue (TB), xylene orange (XO), and phenol red (PR) were used as acid-base indicators. The specificity of the changes in the colorimetric functions of IFCS-I during the absorption of  $\text{NH}_3$  by them was revealed. It was found that the color of the initial IFCS-I samples significantly depended not only on the structure of Ind, but also on the nature of the polybasic hydroxy acid being part of them. The colors of the samples based only on OEDPA (Ind = CoR, BCG, BPB), CA (Ind = CoR, TrOOO, BCG, BPB, BPR, XO) and some MA (TrOOO, BCG) are similar to the colors of aqueous solutions of Brönsted acids. The difference in the colors of the other samples from the colors of strong acid aqueous solutions with the same Ind is apparently due to specific interactions between hydroxy acid anions and neutral dye forms. During “response” to  $\text{NH}_3$  only some IFCS-I samples based on OEDPA (Ind: MO, TrOOO, Az and BPR), CA (Ind: CoR, MR, MO, TrOOO, BXB, BPR, TB, PR) and MA (Ind: LA, MR, MO, Az, BXB, XO, TB, PR) are discolored in contrast to the behavior of  $\text{SO}_2$  indicator chemisorbents.

**Key words:** colorimetry, fibrous chemisorbents, ammonia, acid-base indicators.

**INTRODUCTION.** The service life of any gas filter cartridge (GFC) that cleans polluted air is limited and strongly depends on the operating conditions. Until recently [1], the reaction of the olfactory organ to the appearance of the smell of gas in the space within the mask was widely used for the timely replacement of filters. The above reaction depends on various factors: the composition of the gas mixture, concentration, individual susceptibility of the user, state of health, working conditions, and how quickly the concentration of gases increases, whether the respirator user is familiar with their smell [2, 3]. Different people have a different threshold for perceiving the smell of the same compound. If the gas concentration increases gradually (as the sorbent in the filter is saturated), the sensitivity of the olfactory organ may decrease. Getting used to the smell during long work, colds, concentrating on work – all this makes replacing the filter "by smell" unreliable [4]. In the US, the employer is required to replace the filters on schedule (by calculating [4] or measuring the service life for known working conditions).

A number of authors [1–7] suggest equipping the GFC with an **End of Service Life Indicator (ESLI)**, which would warn the respirator user about the need to replace the GFC; **ESLIs** are passive and active.

For the production of GFC, with which light respirators are equipped, the PCIEHP (Odesa) developed impregnated fibrous chemisorbents of basic gases with visual indication of the moment of dynamic absorption capacity "response" (IFCS-I) [8, 9], obtained by impregnating fibrous carriers with aqueous solutions of polybasic hydroxy acids, to which acid-base indicators (**Ind**) were added. The dynamic absorption capacity "response" of such chemisorbents during the absorption of the basic gas (ammonia) can be visually determined by the change in the

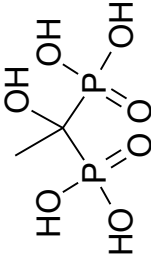
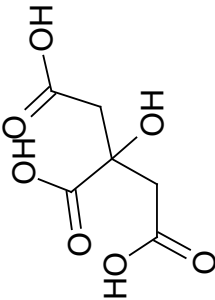
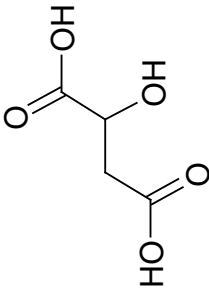
color of the GFC on the side facing the face during the breakthrough of the sorbate.

However, the use of the above-mentioned passive ESLIs has a number of disadvantages described in [6]. To date, there is no theoretical basis for the development of indicator chemisorbents for basic gases, in particular ammonia. Previously, we [6, 10, 11] used digital colorimetry in aqueous solutions and on IFCS-I surfaces to quantitatively characterize the behavior of indicator chemisorbents for acid gases. Therefore, the purpose of this work is to establish the features of the colorimetric behavior of IFCS-I during "response" by  $\text{NH}_3$ , which will become a theoretical basis for the development of active ESLIs. In view of this, the paper presents data on the colorimetric evaluation of IFCS-Is developed by us earlier based on oxyethylenediphosphonic acid (IFCS-OEDPA-I) [8] and citric acid (IFCS-CA-I) [9], as well as of a new IFCS-MA-I based on malic acid (MA).

**EXPERIMENT AND DISCUSSION OF THE RESULTS.** We used for research chemically pure OEDPA, CA та MA (the characteristics of which are given in table 1) without pre-purification, as well as the following Inds, the characteristics of which are given in table 2. As a fibrous carrier (FC) we used non-woven needle-punched filter cloth based on mylar fiber with a thickness of 4.0 mm and a surface density of 470 g/m<sup>2</sup>.

**IFCS-I.** 30 ml of an aqueous solution containing 0.03 mol/l hydroxy acid was placed in a volumetric flask (100 ml) (OEDPA, CA or MA), 0.04 g of Ind was dissolved according to recommendations [12] and brought to the mark with distilled water. The FC was impregnated with obtained solutions at the rate of 8 ml of solution per FC with a diameter of 58 mm until complete absorption. The samples were dried in air at a temperature of 20–25 °C.

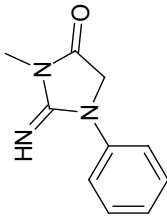
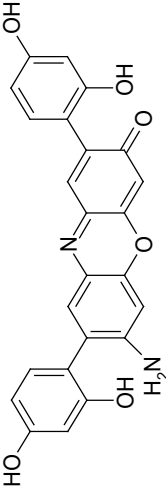
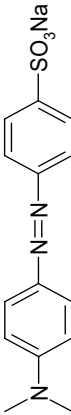
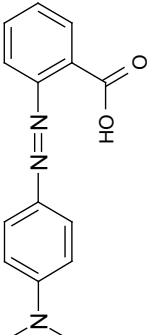
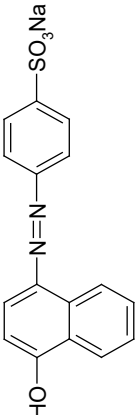
Table 1.  
Physicochemical and toxicological characteristics of polybasic acids.

| Acid                                                                                                                       | M,<br>g/mol | pK <sub>a</sub> | T <sub>melt</sub> ,<br>°C | T <sub>boil</sub> ,<br>°C | P <sub>sv</sub> , Pa<br>(20°C) | lgP <sub>ow</sub> | LD <sub>50</sub> ,<br>mmol/kg | LC <sub>50</sub> ,<br>mmol/(m <sup>3</sup> ·h) | References |
|----------------------------------------------------------------------------------------------------------------------------|-------------|-----------------|---------------------------|---------------------------|--------------------------------|-------------------|-------------------------------|------------------------------------------------|------------|
| <br>Oxyethylnediphosphonic acid (OEDPA) | 206.03      | 1.35            | 198                       | 579                       | NA <sup>***</sup>              | -3.80             | 11.65                         | NA <sup>***</sup>                              | [14-16]    |
|                                                                                                                            |             | 2.87            |                           |                           |                                |                   |                               |                                                |            |
|                                                                                                                            |             | 7.03            |                           |                           |                                |                   |                               |                                                |            |
|                                                                                                                            |             | 11.30           |                           |                           |                                |                   |                               |                                                |            |
| <br>Citric acid (CA)                    | 192.12      | 3.13            | 156                       | 310                       | 2.3·10 <sup>-6</sup>           | -1.64             | 15.62                         | 0.94                                           | [14]       |
|                                                                                                                            |             | 4.76            |                           |                           |                                |                   |                               |                                                |            |
|                                                                                                                            |             | 6.39            |                           |                           |                                |                   |                               |                                                |            |
| <br>Malic acid (MA)                     | 134.09      | 3.51            | 130                       | >225                      | 4.4·10 <sup>-6</sup>           | -1.26             | 26.10                         | 2.43                                           | [14]       |
|                                                                                                                            |             | 5.03            |                           |                           |                                |                   |                               |                                                |            |

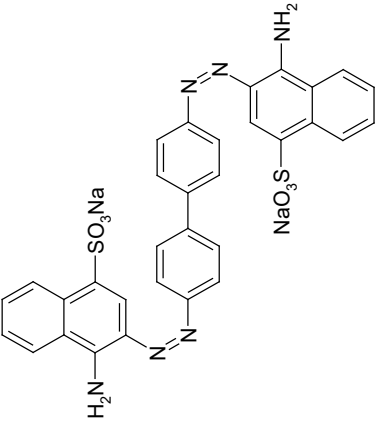
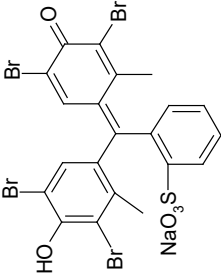
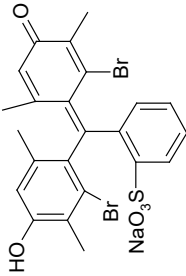
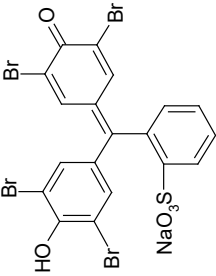
\*rats, orally; \*\* rats, by inhalation; \*\*\*NA – not available.

Table 2.

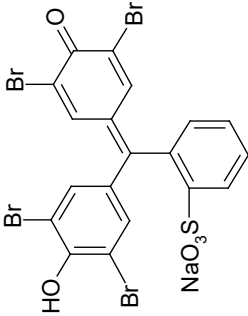
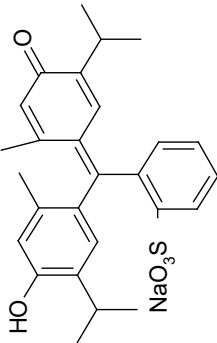
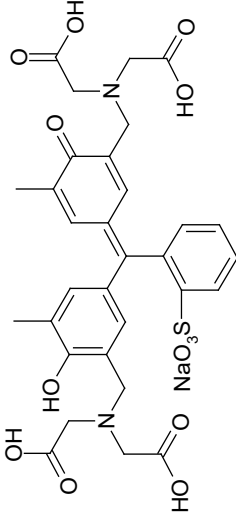
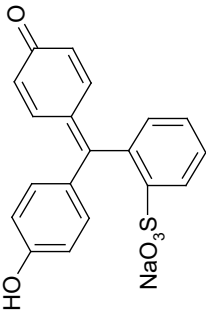
Characteristics of acid-base indicators

| Name              | Abbreviation | Structural formula                                                                   | pK <sub>a</sub>                                                  | Color transition<br>pH range [17] | Color change<br>in aqueous<br>solutions [17] |
|-------------------|--------------|--------------------------------------------------------------------------------------|------------------------------------------------------------------|-----------------------------------|----------------------------------------------|
| <i>I</i>          | <i>2</i>     | <i>3</i>                                                                             | <i>4</i>                                                         | <i>5</i>                          | <i>6</i>                                     |
| Azolitmine        | AZ           |   | 6.40 [18]                                                        | 4.5-8.3                           |                                              |
| Azine dye         |              |                                                                                      |                                                                  |                                   |                                              |
| Lacmoid           | LA           |    | 5.31 [17]                                                        | 4.4-6.4                           |                                              |
| Azo dyes          |              |                                                                                      |                                                                  |                                   |                                              |
| Methyl Orange     | MO           |   | 3.46<br>3.76 [17]                                                | 3.1-4.4                           | Red-orange-<br>yellow                        |
| Methyl Red        | MR           |  | 2.30<br>4.95 [17]                                                | 4.4-6.2                           | Red-yellow                                   |
| Tropaeolin<br>OOO | TrOOO        |  | -0.70 (4'-SO <sub>3</sub> H)<br>2.00 (-N=N-)<br>8.50 (2-OH) [19] | 7.4-8.6<br>10.2-11.8              | amber – orange<br>orange – red               |

Continuation of table 2.

| 1                     | 2   | 3                                                                                    | 4                                                 | 5       | 6                       |
|-----------------------|-----|--------------------------------------------------------------------------------------|---------------------------------------------------|---------|-------------------------|
|                       |     |    |                                                   |         |                         |
| Congo Red             | CoR |                                                                                      | 3.00<br>4.10 [20]                                 | 3.0-5.2 | blue-red-violet         |
| Triphenylmethane dyes |     |                                                                                      |                                                   |         |                         |
|                       |     |    |                                                   |         |                         |
| Bromocresol green     | BCG |                                                                                      | 0.3 (=OH <sup>+</sup> )<br>4.6 (4-OH) [21]        | 3.8-5.4 | yellow – blue<br>-green |
|                       |     |   |                                                   |         |                         |
| Bromoxylene blue      | BXB |                                                                                      | -1.5 (=OH <sup>+</sup> ) [19]<br>6.80 (4-OH) [22] | 6.0-7.6 | yellow – blue           |
|                       |     |  |                                                   |         |                         |
| Bromophenol blue      | BPB |                                                                                      | 0.30 (=OH <sup>+</sup> )<br>4.00 (4-OH) [21]      | 3.0-4.6 | yellow – blue-violet    |

Continuation of table 2.

| 1                  | 2   | 3                                                                                    | 4                                                | 5        | 6                       |
|--------------------|-----|--------------------------------------------------------------------------------------|--------------------------------------------------|----------|-------------------------|
| Bromophenol<br>red | BPR |    | 0.50 (=OH <sup>+</sup> )<br>6.50 (4-OH)<br>[21]  | 5.2-6.8  | yellow – red            |
| Thymol blue        | TB  |    | 1.65 (=OH <sup>+</sup> )<br>8.90 (4-OH)<br>[17]  | 8.0-9.6  | yellow – blue           |
| Xylenol orange     | XO  |   | -1.10 (=OH <sup>+</sup> )<br>6.40 (4-OH)<br>[21] | 6.4-10.4 | yellow – orange-<br>red |
| Phenol red         | PR  |  | 1.20 (=OH <sup>+</sup> )<br>8.40 (4-OH)<br>[21]  | 6.8-8.4  | yellow – red            |

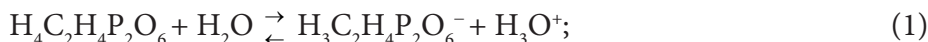
The research was conducted under dynamic conditions using a special gas-dynamic installation described in [13]. The concentration of  $\text{NH}_3$  in the gas-air mixture (GAM) was determined using a Kolion 1B gas analyzer (with calibration for ammonia). The IFCS-I tests were carried out under the conditions of real use of respirators: concentration of  $\text{NH}_3$  in the GAM – 300  $\text{mg}/\text{m}^3$  (15 MPC); relative humidity of the GAM – 90÷95%; GAM flow rate 2.0  $\text{cm}/\text{s}$ . The breakthrough corresponded to the moment of appearance of  $\text{NH}_3$  in the purified GAM behind the material layer at the level of 1–3  $\text{mg}/\text{m}^3$  (MPC = 20  $\text{mg}/\text{m}^3$ ).

The color characteristics of IFCS-I samples (initial samples and those that "response" to  $\text{NH}_3$ ) were evaluated by the method of chemical colorimetry, similarly to [6]. The following colorimetric functions were used:  $R$ ,  $G$ ,  $B$  characteristics;  $X$ ,  $Y$ ,  $Z$  (color coordinates in the system CIEXYZ);  $L$ ,  $A$ ,  $B$  (color coordinates in the equal-contrast system CIELAB),

color saturation ( $S$ ), color tone ( $T$ ), full color difference ( $\Delta E_{76}$ ), yellowness ( $G$ ); the relative whiteness of samples ( $W$ ) and the intensity of the yellow shade ( $K_y$ ). As analytical signals of the "response" of IFCS-I samples, effective absorption in red ( $A_R$ ), green ( $A_G$ ) and blue ( $A_B$ ) colors, as well as the values of total absorption ( $A_T$ ), color ratio ( $C_R$ ) and vector the length in  $RGB$  color space ( $A_v$ ), calculated according to [6, 23], were used.

The color and colorimetric  $RGB$  characteristics for initial IFCS-I samples and those that "responded" to  $\text{NH}_3$  are given in tables 3 and 4.

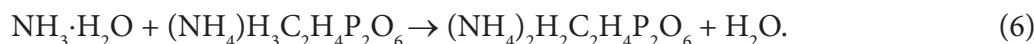
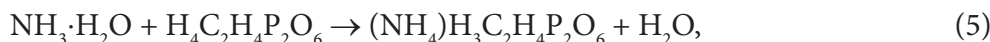
According to the obtained data (Tables 3, 4), the color of the original IFCS-I samples depends significantly not only on the structure of Ind, but also on the nature of the polybasic hydroxy acid being part of them. The presence of hydroxy acids (OEDPA, CA or MA) in the original IFCS-I samples causes an acidic environment on their surface:



which determines their color. However, the color of the samples based only on OEDPA (Ind = CoR, BCG, BPB), CA (Ind = CoR, TrOOO, BCG, BPB, BPR, XO) and some MAs (TrOOO, BCG) is similar to the color of aqueous solutions of Brønsted acids (tables 3, 4). The difference in the color of the rest of the samples from the color of aqueous solutions of strong acids with the same Ind is obviously

caused by specific interactions between hydroxy acid anions and neutral forms of dyes.

*IFCS-OEDPA-I.* Obviously, the chemisorption of ammonia by IFCS-OEDPA-I samples occurs only in the presence of "free" water, as in [24]. At the same time, as a result of acid-base interaction, mono- and disubstituted ammonium salts of OEDPA are formed:



The color of most of the "responded" IFCS-OEDPA-I samples (Ind = Az, MR, TROOO, BCG, BXB, TB, XO and PR), as i IFCS-CA-I (Ind = Az, MR, BXB, TB, XO and PR), is different from the same properties of aqueous alkali solutions (tables 3, 4).

The change in the color of IFCS-OEDPA-I samples with triphenylmethane dyes during "response" to ammonia is caused by Brønsted interactions of various forms of the above Inds with the anions and ammonium cations formed during this process. This is indicated by correlations between the colorimetric functions  $K_{y0}$ ,  $Z_r$  and  $\Delta L$  ( $\Delta L = L_r - L_0$ ) with acid-base characteristics of Ind:

$$K_{y0} = 171,67 - 23,378 \cdot \text{pH}_1; \quad R^2 = 0,9828 \text{ (except BPB and XO),} \quad (7)$$

$$Z_r = -103,89 + 15,536 \cdot \text{pH}_2; \quad R^2 = 0,9360 \text{ (except BKG and XO),} \quad (8)$$

$$\Delta L = 33,839 - 4,4516 \cdot \text{pK}_a; \quad R^2 = 0,9025 \text{ (except BPR and XO).} \quad (9)$$

For initial IFCS-OEDPA-I samples with azo dyes, the colorimetric characteristics  $R_0$ ,  $G_0$  and  $L_0$  simbatically change with the pH values of the lower boundary ( $\text{pH}_1$ ) of the Ind color transition:

$$R_0 = 298,48 - 20,165 \cdot \text{pH}_1; \quad R^2 = 0,9615 \text{ (except CoR),} \quad (10)$$

$$G_0 = 157,71 - 8,252 \cdot \text{pH}_1; \quad R^2 = 0,8892 \text{ (except CoR),} \quad (11)$$

$$L_0 = 80,259 - 4,5119 \cdot \text{pH}_1; \quad R^2 = 0,9987 \text{ (except CoR).} \quad (12)$$

Table 3.

Color of IFCS-I samples.

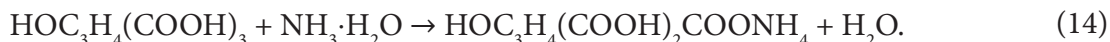
| Ind \ Acid | Initial sample |    |    | "Responded" sample |    |    |
|------------|----------------|----|----|--------------------|----|----|
|            | OEDPA          | CA | MA | OEDPA              | CA | MA |
| Az         |                |    |    |                    |    |    |
| LA         |                |    |    |                    |    |    |
| MO         |                |    |    |                    |    |    |
| MR         |                |    |    |                    |    |    |
| TrOOO      |                |    |    |                    |    |    |
| CoR        |                |    |    |                    |    |    |
| BCG        |                |    |    |                    |    |    |
| BXB        |                |    |    |                    |    |    |
| BPB        |                |    |    |                    |    |    |
| BPR        |                |    |    |                    |    |    |
| TB         |                |    |    |                    |    |    |
| XO         |                |    |    |                    |    |    |
| PR         |                |    |    |                    |    |    |

Table 4.  
Colorimetric functions  $R$ ,  $G$ ,  $B$  of initial IFCS-I samples and those that “responded” to  $\text{NH}_3$ .

| Initial sample |                |     |                |     |                |     |                |     |                |     | Sample that “responded” to NH <sub>3</sub> |     |                |     |                |     |                |     |                |     |                |
|----------------|----------------|-----|----------------|-----|----------------|-----|----------------|-----|----------------|-----|--------------------------------------------|-----|----------------|-----|----------------|-----|----------------|-----|----------------|-----|----------------|
| Am             | OEDPA          | CA  | OEDPA          | CA  | OEDPA          | CA  | OEDPA          | CA  | OEDPA          | CA  | OEDPA                                      | CA  | OEDPA          | CA  | OEDPA          | CA  | OEDPA          | CA  | OEDPA          | CA  |                |
| Ind            | R <sub>0</sub> |     | G <sub>0</sub> |     | B <sub>0</sub> |     | R <sub>t</sub> |     | G <sub>t</sub> |     | B <sub>t</sub>                             |     | R <sub>t</sub> |     | G <sub>t</sub> |     | B <sub>t</sub> |     | G <sub>t</sub> |     | B <sub>t</sub> |
| Az             | 195            | 213 | 88             | 100 | 130            | 123 | 199            | 155 | 100            | 102 | 124                                        | 131 | 167            | -   | -              | 157 | -              | -   | -              | -   |                |
| LA             | 79             | 105 | 61             | 73  | 79             | 95  | 65             | 78  | 65             | 77  | 82                                         | 94  | 63             | -   | 116            | 100 | -              | 135 | -              | 135 |                |
| MO             | 231            | 152 | 138            | 95  | 147            | 107 | 246            | 210 | 196            | 150 | 138                                        | 88  | 117            | 228 | 198            | 118 | 183            | 191 | -              | 191 |                |
| MR             | 220            | 178 | 114            | 81  | 99             | 95  | 230            | 203 | 74             | 103 | 61                                         | 99  | 129            | -   | -              | 27  | -              | -   | -              | -   |                |
| TrOOO          | 146            | 202 | 99             | 72  | 106            | 62  | 185            | 207 | 110            | 97  | 96                                         | 74  | 196            | -   | -              | 156 | -              | -   | -              | -   |                |
| CoR            | 61             | 74  | 91             | 101 | 130            | 128 | 113            | 155 | 63             | 86  | 76                                         | 104 | 167            | 240 | 212            | 7   | 214            | 179 | -              | 179 |                |
| BCG            | 252            | 254 | 209            | 180 | 106            | 81  | 238            | 65  | 161            | 150 | 81                                         | 176 | 88             | 229 | -              | 7   | 187            | -   | -              | -   |                |
| BXB            | 224            | 253 | 210            | 189 | 182            | 110 | 251            | 252 | 148            | 204 | 48                                         | 108 | 108            | 232 | 209            | 99  | 191            | 172 | -              | 172 |                |
| BPB            | 254            | 254 | 159            | 201 | 63             | 107 | 69             | 79  | 113            | 143 | 101                                        | 184 | 3              | 227 | 199            | 15  | 192            | 167 | -              | 167 |                |
| BPR            | 245            | 250 | 29             | 90  | 54             | 54  | 251            | 212 | 81             | 113 | 23                                         | 72  | 152            | 239 | -              | 183 | 166            | -   | -              | -   |                |
| TB             | 202            | 217 | 184            | 149 | 213            | 176 | 217            | 229 | 201            | 215 | 165                                        | 160 | 113            | 214 | -              | 117 | 197            | -   | -              | -   |                |
| XO             | 254            | 253 | 60             | 145 | 42             | 69  | 252            | 191 | 151            | 119 | 56                                         | 93  | 161            | 207 | 178            | 106 | 76             | 110 | -              | 110 |                |
| PR             | 244            | 250 | 132            | 108 | 168            | 98  | 249            | 253 | 153            | 166 | 143                                        | 90  | 214            | 209 | -              | 195 | 169            | -   | -              | 169 |                |

This indicates the Brønsted interaction of OEDPA with the above dyes.

Obviously, during the chemisorption of  $\text{NH}_3$  by IFCS-OEDPA-I samples based on azo indicators, specific non-Brønsted (due to the formation of hydrogen bonds) interactions make a significant contribution to the change in the color of their surface. This is indicated by the absence of correlations between the colorimetric functions of the "responded" samples with the acid-base characteristics of the azo indicators.



At the same time, both the value of the colorimetric characteristic  $y_r$  and relative whiteness ( $W_r$ ) of the "responded" samples, as well as the absolute change of the colorimetric function  $A$  and color tone ( $T$ ) during the "response" of the specified samples to  $\text{NH}_3$  ( $\Delta A = A_r - A_0$ ;  $\Delta T = T_r - T_0$ ) also correlate with  $\text{Ind } pK_a$ :

$$y_r = 0,1507 + 0,028 \cdot pK_{a(4\text{-OH})}; \quad R^2 = 0,9848 \text{ (except BPB)}, \quad (15)$$

$$W_r = 48,544 + 0,5453 \cdot pK_{a(4\text{-OH})}; \quad R^2 = 0,9525 \text{ (except BPB)}, \quad (16)$$

$$\Delta A = 80,452 - 9,3847 \cdot pK_{a(4\text{-OH})}; \quad R^2 = 0,9289, \quad (17)$$

$$\Delta T = -3,1207 + 0,4639 \cdot pK_{a(4\text{-OH})}; \quad R^2 = 0,8958 \text{ (except BCG)}. \quad (18)$$

The colorimetric characteristics of initial IFCS-CA-I samples with azo dyes correlate with the pH values of the lower boundary ( $\text{pH}_1$ ) of Ind color transition:

$$G_0 = -15,538 + 24,477 \cdot \text{pH}_1; \quad R^2 = 0,9916 \text{ (except CoR)}, \quad (19)$$

**IFCS-CA-I.** The coincidence of the color of the initial IFCS-CA-I samples with triphenylmethane dyes described above is accompanied by the following. The intensity of the yellow shade simbatically change with  $\text{Ind } pK_a$ :

$$K_{y_0} = 4,2525 + 11,166 \cdot pK_{a(4\text{-OH})}; \quad R^2 = 0,9694 \text{ (except BCG)}. \quad (13)$$

Taking into account the data in [25, 26], the chemisorption of ammonia by the specified samples (it also occurs in the presence of "free" water) stops at the stage of formation of ammonium dihydrocitrate:

$$S_0 = -1721,6 + 759,01 \cdot \text{pH}_1; \quad R^2 = 0,9922, \quad (20)$$

$$K_{y_0} = 15,834 - 8,8852 \cdot \text{pH}_1; \quad R^2 = 0,9999 \text{ (except CoR)}, \quad (21)$$

$$T_0 = 1,8334 - 0,1206 \cdot \text{pH}_1; \quad R^2 = 0,9944 \text{ (except CoR)}. \quad (22)$$

After the "responded" of the specified samples to  $\text{NH}_3$ , their colorimetric characteristics correlate with the pH values of the upper boundary ( $\text{pH}_2$ ) of Ind color transition:

$$G_r = 53,408 + 9,5405 \cdot \text{pH}_2; \quad R^2 = 0,9763 \text{ (except CoR)}, \quad (23)$$

$$x_r = 0,3699 + 0,0149 \cdot \text{pH}_2; \quad R^2 = 0,9812 \text{ (except CoR)}, \quad (24)$$

$$Z_r = 21,229 - 1,3188 \cdot \text{pH}_2; \quad R^2 = 0,7274, \quad (25)$$

$$\Delta S = 3071,2 - 465,78 \cdot \text{pH}_2; \quad R^2 = 0,9113. \quad (26)$$

An interrelation between the values of the colorimetric function  $Z$  is also observed for initial and "responded" IFCS-CA-I samples with azo dyes:

$$Z_r = 3,7427 + 0,8592 \cdot Z_o;$$

$$R^2 = 0,9947 \text{ (except BXB та BCG), } (27)$$

This testifies to the significant contribution of Brønsted interactions to the change in the



The values of the colorimetric characteristics  $x_r$ ,  $y_r$  and relative whiteness  $W_r$  of “responded” samples IFCS-MA-I with triphenylmethane dyes simabatically change with the pH values of the Ind color transition boundaries:

$$x_r = -73,91 + 13,12 \cdot \text{pH}_2;$$

$$R^2 = 0,8367 \text{ (except BKG, XO), } (29)$$

$$y_r = -62,583 + 11,306 \cdot \text{pH}_2;$$

$$R^2 = 0,8784 \text{ (except BKG, XO), } (30)$$

$$W_r = 2,9346 + 6,6488 \cdot \text{pH}_2;$$

$$R^2 = 0,8551 \text{ (except BPR, BXB). } (31)$$

In the case of azo indicators, the following correlations are observed:

$$x_0 = 0,1274 + 0,0642 \cdot \text{pH}_1;$$

$$R^2 = 0,9225 \text{ (except MO), } (32)$$

$$z_0 = 0,6031 - 0,0726 \cdot \text{pH}_1;$$

$$R^2 = 0,9528 \text{ (except MO), } (33)$$

$$b_r = -54,407 + 12,481 \cdot \text{pH}_1;$$

$$R^2 = 0,9212 \text{ (except MO), } (34)$$

$$K_{g0} = -70,837 + 20,174 \cdot \text{pH}_1;$$

$$R^2 = 0,9601 \text{ (except MO), } (35)$$

$$A_G = -0,3895 + 0,0534 \cdot \text{pH}_1;$$

$$R^2 = 0,942 \text{ (except CR), } (36)$$

$$\Delta S = 3065,7 - 469,92 \cdot \text{pH}_2;$$

$$R^2 = 0,9067, \quad (37)$$

$$\Delta E = 126,48 - 18,319 \cdot \text{pH}_2;$$

$$R^2 = 0,9884 \text{ (except TROOO). } (38)$$

In addition, the following correlations are observed between the colorimetric characteristics of IFCS-OEDPA-I and IFCS-CA-I samples:

surface color of the samples IFCS-CA-I during the chemisorption of ammonia by them.

**IFCS-MA-I.** Ammonia chemisorption by IFCS-MA-I samples is caused by the formation of ammonium hydromalate:

$$R_{\text{OEDPA}} = -26,404 + 1,0711 \cdot R_{\text{CA}};$$

$$R^2 = 0,9826, \quad (39)$$

$$X_{\text{OEDPA}} = -4,3135 + 1,051 \cdot X_{\text{CA}};$$

$$R^2 = 0,9047 \text{ (except MP and MO). } (40)$$

On the basis of colorimetric data processing, it was established that during the “response” to ammonia of IFCS-I samples with triphenylmethane dyes based on hydroxycarboxylic acids (CA and MA), effective absorption in red (AR), green (AG) colors and vector length in the RGB (Av) color space are related as follows:

$$A_{R(\text{MA})} = -0,0265 + 0,9738 \cdot A_{R(\text{CA})};$$

$$R^2 = 0,9846 \text{ (except BPR); } (41)$$

$$A_{G(\text{MA})} = -0,0098 + 1,0975 \cdot A_{G(\text{CA})};$$

$$R^2 = 0,9667 \text{ (except XO); } (42)$$

$$A_{v(\text{MA})} = 2,6625 + 0,8914 \cdot A_{v(\text{CA})};$$

$$R^2 = 0,9679 \text{ (except BPR). } (43)$$

For IFCS-OEDPA-I and IFCS-MA-I samples with azo dyes, the following dependencies are observed:

$$\Delta E_{76(\text{MA})} = -35,819 + 2,1256 \cdot \Delta E_{76(\text{OEDPA})};$$

$$R^2 = 0,9758; \quad (44)$$

$$A_{v(\text{MA})} = -90,85 + 4,4172 \cdot A_{v(\text{OEDPA})};$$

$$R^2 = 0,9650. \quad (45)$$

**CONCLUSIONS.** During “response” to  $\text{NH}_3$ , only some IFCS-I samples (table 3, 4) based on OEDPA (Ind: MO, TrOOO, Az and BPR), CA (Ind: CoR, MR, MO, TrOOO, BPR, BXB, TB, PR) and MA (Ind: LA, MR, MO, Az, BXB, XO, TB, PR) are decolorized, in contrast to the

behavior of  $\text{SO}_2$  indicator chemisorbents [6]. As an analytical signal of the "response" IFCS-I samples to  $\text{NH}_3$ , we chose the value of total absorption, similarly to [6], the absolute value of which for IFCS -OEDPA-I and IFCS-CA-I decreases in the series of indicators:

$\text{XO} < \text{MO} < \text{TrOOO} < \text{BPR} < \text{PR} < \text{LA} < \text{TB} < \text{CoR} < \text{BCG} < \text{MR} < \text{BPB} < \text{BXB};$   
 $\text{MO} < \text{TrOOO} < \text{MR} < \text{CoR} < \text{PR} < \text{BPR} < \text{TB} < \text{BXB} < \text{XO} < \text{Az} < \text{LA} < \text{BCG} < \text{BPB};$   
 $\text{PR} < \text{LA} < \text{TB} < \text{TrOOO} < \text{BXB} < \text{MR} < \text{AZ} < \text{XO} < \text{MO} < \text{BPR} < \text{BPB} < \text{BXG} < \text{CoR}.$

Thus, the specificity of the change in the colorimetric functions of impregnated fibrous

indicator chemisorbents during the absorption of  $\text{NH}_3$  by them was revealed. The change in the color of IFCS-I samples is caused by both the Brønsted mechanism and specific interactions (due to the formation of hydrogen bonds).



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### ІМПРЕГНОВАНІ ВОЛОКНИСТІ ХЕМОСОРБЕНТИ ДЛЯ КОЛЬОРОМЕТРИЧНОГО ДЕТЕКТУВАННЯ АМІАКУ

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У роботі наведено результати досліджень особливостей колориметричної поведінки імпрегнованих волокнистих хемосорбентів (IFCS) основних газів із візуальною ідентифікацією моменту «спрацьовування» ди-

намірної поглинальної ємності (IFCS-I) при поглинанні аміаку. Хемосорбенти одержано шляхом просочування волокнистих носіїв водними розчинами багатоосновних гідроксикислот, до складу яких додавали кислотно-основні індикатори (Ind). Як об'єкти досліджень використовували IFCS-I на основі оксиетилендифосфонової (IFCS-OEDPA-I), лимонної (IFCS-CA-I) та яблучної (IFCS-MA-I) кислот. Як кислотно-основні індикатори було використано наступні: азолітмін (Az), лакмоїд (LA), метиловий оранжевий (МО), метиловий червоний (MR), тропеолін ООО (TrOOO), конго червоний (CoR), бромкрезоловий зелений (BCG), бромксиленоловий синій (BXB), бромфеноловий синій (BPB), бромфеноловий червоний (BPR), тимоловий синій (TB), ксиленоловий оранжевий (ХО) та феноловий червоний (PR). Виявлено специфіку зміни колориметричних функцій IFCS-I під час поглинання ними  $\text{NH}_3$ .

Встановлено що забарвлення вихідних зразків IFCS-I суттєво залежить не лише

від будови Ind, а й від природи багато-основної гідроксикислоти, що входить до їхнього складу. Забарвлення зразків на основі лише OEDPA (Ind = CoR, BCG, BPB), CA (Ind = CoR, TrOOO, BCG, BPB, BPR, XO) та деяких MA (TrOOO, BCG) подібне до забарвлення водних розчинів бренстедівських кислот. Відмінність забарвлення решти зразків від забарвлення водних розчинів сильних кислот з одними й тими ж Ind, вочевидь, спричинена специфічними взаємодіями між аніонами гідроксикислот і нейтральними формами барвників. Під час «спрацювання» по  $\text{NH}_3$  відбувається знебарвлення лише деяких зразків IFCS-I на основі OEDPA (Ind: MO, TrOOO, Az та BPR), CA (Ind: CoR, MR, MO, TrOOO, BXB, BPR, TB, PR) та MA (Ind: LA, MR, MO, Az, BXB, XO, TB, PR), на відміну від поведінки індикаторних хемосорбентів  $\text{SO}_2$ .

**Ключові слова:** кольориметрія, волокнисті хемосорбенти, аміак, кислотно-основні індикатори.

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