THE IMPREGNATED FIBROUS CHEMISORBENTS FOR COLORIMETRIC DETECTION OF THE SULFUR DIOXIDE

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The paper presents the research results on the colorimetric behavior of impregnated fibrous chemisorbents (IFCS-I) of acid gases with visual identification of the dynamic absorption capacity “response” moment during the absorption of sulfur dioxide. Chemisorbents were obtained by impregnation of fibrous carriers by N-containing organic bases aqueous solutions with adding acid-base indicators (Ind). IFCS-I based on hexamethylenetetramine (IFCS-HMTA-I) and polyethylene-polyamine (IFCS-PEPA-I), as well as IFCS-MEA-EDTA-I based on monoethanolamine (MEA) and the disodium salt of ethylenediaminetetraacetic acid (EDTA) were used. The change specificity of colorimetric functions of indicator impregnated fibrous chemisorbents during their absorption of SO2 is revealed. IFCS-I original samples color significantly depends not only on the structure of Ind, but also the nature of amines (MEA, HMTA and PEPA), which are part of them. The color of the “response” samples of IFCS-MEA-EDTA-I, IFCS-PEPA-I and IFCS-HMTA-I, differ from the same properties of Bronsted acids aqueous solutions. The color change of azo-indicators occurs due to redox reactions with sulfite compounds. PEPA molecules and their ammonium cations in the composition of IFCS-I stabilize azo-indicators to these redox transformations.

Key words: colorimetry, fibrous chemisorbents, sulfur dioxide, acid-base indicators.

INTRODUCTION. When using known respirators, the moment of their “response” is determined by the workers of labor protection departments on the basis of data on the absorption capacity of gasfiltering elements (GFEs). The difficulty of the work done by the user into two ways: the results of instrumental measurements of the air pollution level during the operation of the respirator by the user, or by organoleptic method. In the former case, a special equipment and trained personnel are required to obtain the necessary information, and in the latter case, the moment of “breakthrough” is determined subjectively and can lead to the poisoning of the user. That is, a significant disadvantage of known filtering
respirators, designed for protection against toxic acid gases, is the impossibility to determine in proper time the moment of dynamic absorption capacity “response” of the GFE, to note the breakthrough of sorptive into the mask cavity.

The authors of [1,2] proposed granular indicator chemisorbents - ionites, which change their color during “response” to NH₃, H₂S, SO₂, HCl, etc, for fitting up gas filter boxes and gas sample preparation filters in the manufacture of gas analyzers. The ionite filter body is made by casting from an optically transparent shock-resistant polymer material (polycarbonate fluoroplastic), which makes it possible to watch the condition of chemiosorbent during the “response” of the filter.

Belarusian colleagues [3] proposed indicator materials for SO₂ capture, obtained by impregnating a fibrous anionite containing in its structure functional groups of tertiary amine (dimethylaminopropylamine) with acid – base indicators in a pH range of 7.0–8.5.

To make GFEs, with which light respirators are fitted, the Physico-Chemical Institute of Environment and Human Protection of MES of Ukraine and NAS of Ukraine (Odesa) has developed impregnated fibrous chemisorbents of acid gases with visual identification of the moment of dynamic absorption capacity “response” (IFCS-I) [4–6], obtained by impregnating fibrous carriers with aqueous solutions of N-containing organic bases (Am: monoethanolamine (MEA), hexamethylenetetramine (HMTA) and polyethylenepolyamine (PEPA)), to which acid-base indicators (Ind) with wider color transition range between pH 5.0 and 9.2 were added.

The “response” of the dynamic absorption capacity of such chemisorbents during the absorption of an acid gases (sulfur dioxide) can be visually determined from GFE color change on the side facing the face during the “breakthrough” of sorptive.

However, the visual indication of dynamic absorption capacity “response” has only a qualitative characteristic. The analytical signal obtained by the visual detection of the color change of GFE samples (IFCS-I) allows only to note the moment of “breakthrough” of toxic chemisorptive (SO₂). The comparison of indicator systems by the intensity of color change to choose ones that are more suitable for practical use can be only made at the qualitative level.

Besides this, digital colorimetry in aqueous solutions and on different surfaces is use in addition to spectrophotometry to solve different chemical and analytical problems [7–12]. However, there is no theoretical basis today for the development of indicator chemisorbents of acid gases such as sulfur dioxide. Therefore, the aim of this work to determine the peculiarities of colorimetric behavior of IFCS-I during “response” to SO₂. In view of this, this paper presents data on the colorimetric assessment of IFCS-I’s based on hexamethylenetetramine (IFCS-HMTA-I) [5] and polyethylenepolyamine (IFCS-PEPA-I) [4], developed by us earlier, as well as a new IFCS-MEA-EDTA-I based on a chemisorbent with prolonged action [12], which contains MEA and a disodium salt of ethylenediaminetetraacetic acid (EDTA).

EXPERIMENT AND DISCUSSION OF THE RESULTS. To carry out the research, we used chemically pure MEA and EDTA “reagent grade”, HMTA “pharmacopoeial”, PEPA (CAS 23920-38-5) without pre-purification, as well as Inds, whose characteristics are listed in Table 1. As a fibrous carried (FC) we used a thickness of 2.2 mm and a surface density of 390 g/m², for filtration.
IFCS-MEA-EDTA-I. 0.02 g of Ind was dissolved in 50 ml of an aqueous solution containing 0.30 mol/L MEA and 0.02 mol/L EDTA. The FC was impregnated with the resulting solution at the rate of 56.3 mL of solution per 10 g of carrier until full suction. The samples were air dried at 20-25°C.

IFCS-PEPA-I, IFCS-HMTA-I. The impregnation solutions were prepared according to [5,6], and the FC was impregnated with them similarly to IFCS-MEA-EDTA-I.

The research was carried out under dynamic conditions by means of a special gas dynamic installation, described in [14]. The concentration of SO\textsubscript{2} in the gas-air mixture (GAM) was determined by means of an electrochemical gas analyzer 667 EKh 10 (Ukranalyt LLC). IFCS-I was tested under the real use condition of respirators: SO\textsubscript{2} concentration in the GAM: 150 mg/m\textsuperscript{3} (MPC), relative humidity of the GAM: 90-95%, GAM flow rate: 2.0 cm/s. The breakthrough correspondent to the moment of appearance of SO\textsubscript{2} in the purified GAM behind the layer of material at a level of 1–3 mg/m\textsuperscript{3} (MPC=10 mg/m\textsuperscript{3}).

The color characteristics of IFCS-I samples (initial and “responded” to SO\textsubscript{2}) were estimated by the method of chemical colorimetry [11] by processing the data from the flatbed scanner in an A4 black and white multifunction device (HP Laser 13) using the True Color mode (16.5 million color shades), optical resolution 600 dpi (increasing the resolution to 1200 dpi gave no improvement of image characteristics). The averaged values of the \(R, G, B\) characteristics of samples under investigation were determined using the on line program IMGonline [15]. The following colorimetric functions were used: \(X, Y, Z\) (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 (\(G\)), calculated according to [6]; relative whiteness of samples (\(W\)) and intensity of yellow hue (\(K_y\)) [12].

As analytical signals of “response” of IFCS-I samples we also used effective absorption in the red (\(A_r\)), green (\(A_g\)), and blue (\(A_b\)) ranges, whose values were calculated from formulas similar to those in [16]:

\[
A_r = -\log(R / R_0); \tag{1}
\]
\[
A_g = -\log(G / G_0); \tag{2}
\]
\[
A_b = -\log(B / B_0), \tag{3}
\]

Where \(R_0, G_0, B_0\) are the color coordinates of initials samples; \(R_r, G_r, B_r\) are the color coordinates of “responded” samples. The values of total absorption (\(A_T\)) and color ratio (\(CR\)) were determined similarly to [16]:

\[
A_T = A_r + A_g + A_b; \tag{4}
\]
\[
CR = R_r / R_0 + G_r / G_0 + B_r / B_0 \tag{5}
\]

The color sang colorimetric RGB characteristics for original IFCS-I samples and those that “responded” to SO\textsubscript{2} are listed in Tables 2 and 3.

Results and discussion

According to the data obtained (Tables 2,3), the color of original IFCS-I samples depends largely not only on the structure of Ind, but also on the nature of Am, which are part of them. The presence of Am in original IFCS-I samples causes the basicity of their surface:

\[
\text{Am} + \text{H}_2\text{O} \overset{\leftrightarrow}{\longrightarrow} \text{AmH}^+ + \text{OH}^-, \tag{6}
\]

which causes coloring. However, the color of samples based only PEPA (Ind = TrOO, TrOOO, BCY, BCP, BXB, BPB, BPR and CrR)
and some MEAs (Ind = BXB) and HMTAs (AL, BXB) is similar to that of aqueous alkaline solutions (Table 1,2). The difference of the color of the other samples from that of aqueous alkaline solutions with the same Ind is apparently due to specific interactions between ammonium cations and anionic forms of dyes.

**IFCS-MEA-EDTA-I**

The chemisorption of sulfur dioxide by IFCS-MEA-EDTA-I samples takes place only in the presence of “free” water. In this case, “ammonium” sulfites, hydrosulfites and pyrosulfites are formed as a result of acid – base interaction [17,18]:

\[
\text{SO}_2 + n\text{H}_2\text{O} \leftrightarrow \text{SO}_2\cdot\text{H}_2\text{O} + (n-1)\text{H}_2\text{O}, \quad (7)
\]

\[
\text{SO}_2\cdot\text{H}_2\text{O} + 2\text{HOCH}_2\text{CH}_2\text{NH}_2 \rightarrow [\text{HOCH}_2\text{CH}_2\text{NH}_3]^+_2\text{SO}_3^-, \quad (8)
\]

\[
[\text{HOCH}_2\text{CH}_2\text{NH}_3]^+_2\text{SO}_3^- + \text{SO}_2\cdot\text{H}_2\text{O} \leftrightarrow 2[\text{HOCH}_2\text{CH}_2\text{NH}_3]^+_2\text{HSO}_3^-, \quad (9)
\]

\[
2[\text{HOCH}_2\text{CH}_2\text{NH}_3]^+_2\text{HSO}_3^- + (n-2)\text{H}_2\text{O} \rightarrow [\text{HOCH}_2\text{CH}_2\text{NH}_3]^+_2\text{S}_2\text{O}_5^- + (n-1)\text{H}_2\text{O}. \quad (10)
\]

Comparison of the data presented in [13] shows that the presence of EDTA in IFCS-I samples determines the degree of “response” of MEA to SO\(_2\) owing to the deeper transformation of the latter with increasing the fraction of hydrosulfites and pyrosulfites similar to [18]. The colors of “responded” IFCS-MEA-EDTA-I samples, like IFCS-PEPA-I and IFCS-HMTA-I, differ from the same properties of aqueous solutions of Brönsted acids (Tables 1,2)

| **Table 1** |
|---|
| **Characteristics of acid-base indicators** |
| Name | Abbreviation | Structure | \(pK_a\) | The pH range of the color transition [18] | Color change in aqueous solutions [18] |
|---|---|---|---|---|---|
| Azolitmine | AZ | 6,4 [20] | 4,5-8,3 |
| Anthraquinone dye |
| Alizarin | AL | 6,0; 12,5 [21] | 5,5-6,8 10,1-12,1 | yellow – dark pink dark pink – purple |
### Table 1

| Azine dye | Azo dyes |
|-----------|----------|
| Lacmoid   | Methyl Orange |
| LA        | MO       |
| ![Diagram](lacmoid.png) | ![Diagram](methyl-orange.png) |
| 5,31 [19] | 3,1-4,4 red – orange-yellow |
| 4,4-6,4   |          |

| Methyl Red | Tropaeolin O |
| MR        | TrO       |
| ![Diagram](methyl-red.png) | ![Diagram](tropaeolin-o.png) |
| 4,4-6,2   | -0,8 (4’-SO3H)  |
| red – yellow | 11,0-12,7 yellow – red |
| 0,5 (-N=N-) | 0,5 (2-OH) |
| 6,5 (2-OH) | 6,5 (2-OH) [21] |

| Tropaeolin OO | TrOO |
| ![Diagram](tropaeolin-oo.png) | ![Diagram](tropaeolin-ooo.png) |
| -0,6 (4’-SO3H) | -0,7 (4’-SO3H) |
| 1,3-3,2 red – yellow | 7,4-8,6 amber – orange |
| 0,8 (-N=N-) | 2,0 (-NH-) |
| 2,0 (-NH-) [22] | 2,0 (-NH-) [23] |

| Tropaeolin OOO | TrOOO |
| ![Diagram](tropaeolin-oooo.png) | ![Diagram](tropaeolin-ooooo.png) |
| 7,4-8,6 amber – orange | 7,4-8,6 amber – orange |
| 10,2-11,8 red | 10,2-11,8 red |
| 2,0 (-N=N-) | 2,0 (-N=N-) |
| 2,0 (-N=N-) [23] | 2,0 (-N=N-) [23] |

| Congo Red | CoR |
| ![Diagram](congo-red.png) | ![Diagram](congo-red.png) |
| 3,0 | 3,0-5,2 yellow blue-red – purple |
| 4,1 [22] | |
|   | 1       | 2       | 3       | 4       | 5         | 6         |
|---|---------|---------|---------|---------|-----------|-----------|
|  | **Triphenylmethane dyes**                      |         |         |         |           |           |
|  | **Bromocresol green**                          | BCG     |         | 0,3 (=OH\(^+\)) | 3,8-5,4  | yellow – blue-green |
|  | ![Bromocresol Green](image)                     |         |         | 4,6 (4-OH) [21]  |           |           |
|  | **Bromocresol purple**                          | BCP     |         | 0,4 (=OH\(^+\)) | 5,2-6,8  | yellow – purple |
|  | ![Bromocresol Purple](image)                    |         |         | 6,5 (4-OH) [21]  |           |           |
|  | **Bromoxylenol blue**                           | BXB     |         | -1,5 (=OH\(^+\)) | 6,0-7,6  | yellow – blue |
|  | ![Bromoxylenol Blue](image)                     |         |         | 6,80 (4-OH) [24] |           |           |
|  | **Bromophenol blue**                            | BPB     |         | 0,3 (=OH\(^+\)) | 3,0-4,6  | yellow – blue-violet |
|  | ![Bromophenol Blue](image)                      |         |         | 4,0 (4-OH) [21]  |           |           |
|  | **Bromophenol red**                             | BPR     |         | 0,5 (=OH\(^+\)) | 5,2-6,8  | yellow – red |
|  | ![Bromophenol Red](image)                       |         |         | 6,5 (4-OH) [21]  |           |           |
|     | 1            | 2            | 3                      | 4              | 5          | 6                        |
|-----|--------------|--------------|------------------------|----------------|------------|--------------------------|
| 1   | Bromothymol blue | BTB         | ![Bromothymol blue](image) | 0,5 (=OH⁺)    | 6,0-7,6   | yellow – blue            |
| 2   | Cresol red   | CrR         | ![Cresol red](image)   | 1,5 (=OH⁺)    | 0,2-1,8   | red – yellow             |
|     |              |             |                        | 8,1 (4-OH)    | 7,0-8,8   | yellow – red – dish-pur- |
| 3   | Xylenol orange | XO         | ![Xylenol orange](image) | -1,1 (=OH⁺)   | 6,4-10,4  | yellow – orange-red      |
| 4   | Xylenol blue | XB          | ![Xylenol blue](image) | 1,5 (=OH⁺)    | 1,2-2,8   | red – yellow – dish-pur- |
|     |              |             |                        | 9,5 (4-OH)    | 8,0-9,6   | yellow – red – blue      |
| 5   | Phenol red   | PR          | ![Phenol red](image)   | 1,2 (=OH⁺)    | 6,8-8,4   | yellow – red             |
|     |              |             |                        | 8,4 (4-OH)    |            |                           |
### Table 2

| Ind | Am | MEA | PEPA | HMTA | MEA | PEPA | HMTA |
|-----|----|-----|------|------|-----|------|------|
| Az  | -  | -   | -    | -    | -   | -    | -    |
| AL  | -  | -   | -    | -    | -   | -    | -    |
| LA  | -  | -   | -    | -    | -   | -    | -    |
| MO  | -  | -   | -    | -    | -   | -    | -    |
| MR  | -  | -   | -    | -    | -   | -    | -    |
| TrO | -  | -   | -    | -    | -   | -    | -    |
| TrOO| -  | -   | -    | -    | -   | -    | -    |
| TrOOO| - | -  | -    | -    | -   | -    | -    |
| CoR | -  | -   | -    | -    | -   | -    | -    |
| BCG | -  | -   | -    | -    | -   | -    | -    |
| BCP | -  | -   | -    | -    | -   | -    | -    |
| BXB | -  | -   | -    | -    | -   | -    | -    |
| BPB | -  | -   | -    | -    | -   | -    | -    |
| BPR | -  | -   | -    | -    | -   | -    | -    |
| BTB | -  | -   | -    | -    | -   | -    | -    |
| CrR | -  | -   | -    | -    | -   | -    | -    |
| XO  | -  | -   | -    | -    | -   | -    | -    |
| XB  | -  | -   | -    | -    | -   | -    | -    |
| PR  | -  | -   | -    | -    | -   | -    | -    |

The color version of the table can be viewed in the online version of the journal [https://ucj.org.ua/index.php/journal](https://ucj.org.ua/index.php/journal)

Abbreviation **Ind** see **Table 1**

MEA – monoethanolamine; HMTA – hexamethylenetetramine; polyethylenepolyamine – PEPA
| Am | MEA | PEPA | HMTA | MEA | PEPA | HMTA | MEA | PEPA | HMTA | MEA | PEPA | HMTA | MEA | PEPA | HMTA |
|----|-----|------|------|-----|------|------|-----|------|------|-----|------|------|-----|------|------|
| Ind | $R_o$ | $G_o$ | $B_o$ | $R_i$ | $G_i$ | $B_i$ |
| Az  | 98  | -    | 141  | -   | 159  | -   | 168 | -    | 167  | -   | 157  | -    | -   | -    |
| Al  | 115 | -    | 94   | 59  | -    | 90  | 115 | -    | 155  | -   | 128  | -    | 147 | 63   | -    |
| L   | 75  | 1    | 119  | 85  | 173  | 173 | 95  | 254  | 177  | 105 | 178  | 195  | 117 | 228  | 198  |
| MO  | 252 | -    | 98   | -   | 3    | -   | 250 | -    | 129  | -   | 27   | -    | -   | -    |
| MR  | 252 | -    | 123  | -   | 1    | -   | 234 | -    | 196  | -   | 156  | -    | -   | -    |
| TrO | 237 | 255  | 234  | 122 | 254  | 221 | 4   | 1    | 78   | 245 | 233  | 202  | 167 | 240  | 212  |
| TrOO| 242 | 254  | -    | 76  | 9    | 5   | 47  | -    | 245  | 229 | -    | 88   | 229 | -    | 7    |
| TrOOO| 221 | 254  | 208  | 8   | 58   | 69  | 36  | 86   | 95   | 209 | 240  | 212  | 108 | 232  | 209  |
| CoR | 248 | 254  | 195  | 3   | 44   | 87  | 20  | 70   | 97   | 244 | 226  | 195  | 3   | 227  | 199  |
| BCG | 17  | 1    | -    | 112 | 169  | -   | 189 | 131  | -    | 79  | 206  | -    | 152 | 239  | -    |
| BCP | 38  | 172  | -    | 61  | 97   | -   | 146 | 201  | -    | 101 | 199  | -    | 113 | 214  | -    |
| BXB | 14  | 1    | 30   | 84  | 72   | 95  | 163 | 193  | 165  | 122 | 137  | 152  | 161 | 207  | 178  |
| BPB | 17  | -    | 2    | 66  | -    | 157 | 169 | -    | 254  | 200 | -    | 210  | 184 | 214  | 209  |
| BPR | 54  | 254  | -    | 37  | 114  | -   | 132 | 215  | -    | 76  | 254  | -    | 102 | 114  | -    |
| BTB | 46  | 1    | 68   | 120 | 229  | 144 | 169 | 250  | 165  | 92  | 182  | 178  | 144 | 220  | 193  |
| CrR | 121 | 100  | 90   | 38  | 68   | 87  | 102 | 202  | 116  | 226 | 202  | 182  | 113 | 97   | 173  |
| XO  | 138 | 104  | -    | 72  | 66   | -   | 102 | 149  | -    | 188 | 215  | -    | 122 | 192  | -    |
| XB  | -   | 8    | 183  | -   | 223  | 118 | -   | 228  | 193  | -   | 217  | 193  | -   | 217  | 199  |
| PR  | -   | -    | -    | -   | -    | -   | -   | -    | -    | -   | -    | -    | -   | -    | -    |

Abbreviation **Ind** see Table 1

MEA – monoethanolamine; HMTA – hexamethylenetetramine; polyethylene polyamine – PEPA
For IFCS-MEA-EDTA-I samples with triphenylmetane dyes, the colorimetric characteristics $X_r$, $Z_r$, $\Delta S$ and $A_r$ change symmetrically with the pH values of the lower limit ($pH_1$) of Ind color transition:

$$X_r = -55,72 + 13,11 \cdot pH_1; \quad R^2 = 0,9304; \quad n = 6 \text{ (except BXB)},$$  \hspace{1cm} (11)

$$\Delta S = -18270 + 2952 \cdot pH_1; \quad R^2 = 0,9640; \quad n = 6 \text{ (except BCG)},$$  \hspace{1cm} (13)

$$A_r = -1,663 + 0,2168 \cdot pH_1; \quad R^2 = 0,8957; \quad n = 6 \text{ (except BXB)},$$  \hspace{1cm} (14)

And $G_r$, $\Delta S$ and $A_r$ with $pK_{4-OH}$ values:

$$G_r = -486,7 + 77,06 \cdot pK_{4-OH}; \quad R^2 = 0,9468; \quad n = 6 \text{ (except BPR)},$$  \hspace{1cm} (15)

$$\Delta S = -21290 + 2966 \cdot pK_{4-OH}; \quad R^2 = 0,9696; \quad n = 6 \text{ (except BCG)},$$  \hspace{1cm} (16)

$$A_r = -1,746 + 0,1969 \cdot pK_{4-OH}; \quad R^2 = 0,8354; \quad n = 6 \text{ (except BXB)},$$  \hspace{1cm} (17)

The above-described coloring of initial IFCS-PEPA-I samples with azo dyes in accompanied by the following: yellow ness changes antebatelly to and relative whiteness symmetrically with the pH values of the upper limit ($pH_2$) of Ind color transition:

$$G_0 = 266,7 - 12,81 \cdot pH_2; \quad R^2 = 0,9286; \quad n = 5,$$  \hspace{1cm} (18)

$$W_0 = 34,19 + 2,441 \cdot pH_2; \quad R^2 = 0,9584; \quad n = 5.$$  \hspace{1cm} (19)

Taking into account the data presented in [18], the chemisorption of sulfur dioxide by the above samples under static and dynamic condition (takes place in the presence of “free” water too) stops at the stage of formation of polyammonium sulfites:

$$2NH_2(CH_2CH_2NH)_nH + (n+1)SO_4^2- + (n+1)H_2O \rightarrow [NH_2(CH_2CH_2NH)_nH]_2(SO_3^2-)_{n+1}.$$  \hspace{1cm} (20)

In this case, the following relations are observed:

$$W_r = 82,14 + 0,572 \cdot pH_2; \quad R^2 = 0,9381; \quad n = 5,$$  \hspace{1cm} (21)

$$\Delta E_76 = 101,3 - 1,524 \cdot pH_2; \quad R^2 = 0,8574; \quad n = 5,$$  \hspace{1cm} (22)

$$\Delta W = 47,95 - 1,869 \cdot pH_2; \quad R^2 = 0,9312; \quad n = 5.$$  \hspace{1cm} (23)

The aforesaid indicates the stabilization of azo indicators by PEPA molecules and their ammonium cations in terms of the occurrence of redox reactions. The color change in this case occurs by the Brönsted mechanism.

IFCS-HMTA-I

The chemisorption of sulfur dioxide by IFCS-HMTA-I samples occurs through condensation (accompanied by the oxidation $S(IV) \rightarrow S(VI)$), which involves the acid-catalyzed hydrolysis of HMTA to form aminomethanesulfonic acid (AMSA) [26]:

$$2NH_2(CH_2CH_2NH)_nH + (n+1)SO_4^2- + (n+1)H_2O \rightarrow [NH_2(CH_2CH_2NH)_nH]_2(SO_3^2-)_{n+1}.$$  \hspace{1cm} (20)
In this case, the colorimetric characteristics $G_r$ and $K_{gr}$ of “responded” IFCS-HMTA-I samples (Ind = triphenylmethane dyes) change antably to pH$_1$ values:

$$G_r = 290,7 - 40,74 \cdot \text{pH}_1; \quad R^2 = 0,9236; \quad (25)$$

$$K_{gr} = 250,5 - 36,061 \cdot \text{pH}_1; \quad R^2 = 0,9786; \quad (26)$$

This indicates the formation of ion associates between AMSA zwitterions and the anionic forms of the above indicators.

With increase in the pH values of the color transition limit of azo indicators for HMTA-based IFCS samples, $\Delta S$ decreased (unlike IFCS-MEA-EDTA-I samples with triphenylmethane dyes):

$$\Delta S = -93,78 - 364,7 \cdot \text{pH}_2; \quad R^2 = 0,9976; \quad (27)$$

$$\Delta S = -812,5 - 347,5 \cdot \text{pH}_1; \quad R^2 = 0,9792; \quad (28)$$

**CONCLUSION.** During the “response” of IFCS-I samples to SO$_2$, their decoloration takes place (Table 2,3) as indicated by the positive values of $W$ and negative values of $A_T$. As the analytical signal of the “response” of IFCS-I samples we chose the amount of total absorption whose absolute value for IFCS-MEA-EDTA-I, IFCS-PEPA-I and IFCS-HMTA-I decreased in the orders of indicators:

MR > TOO > MO ≈ BXB > BCG > BPR > BCP > TOO > LA > XO > AZ > BTB > TOO;

T0 ≈ BCG > BPB > TOO > BXB > BTB > XB > CoR > TOOO > XO > BCP > CrR > BPR;

BXB > TOOO > XO > CoR > BTB > BPB > LA > TO > AL > PB.

Thus, the specificity of change in the colormetric function of indicator impregnated fibrous chemisorbents during the absorption of SO$_2$ by then has been established. The color change of IFCS-MEA-EDTA-I samples with triphenylmethane dyes occurs by the Brønsted mechanism and that of azo indicators through redox reactions with sulfite compounds. The PEPA molecules and their ammonium cations in IFCS-I stabilize azo indicators up to the above redox transformations. For deeper conclusions, an additional study of behavior in SO$_2$-Am-Ind-H$_2$O model system is needed, which will be the subject of our future research.

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ІМПРЕГНОВАНІ ВОЛОКНИСТІ ХЕМОСОРБЕНТИ ДЛЯ КОЛОРИМЕТРИЧНОЇ ДЕТЕКЦІЇ ДІОКСИДУ СІРКИ

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У роботі наведено результати досліджень особливостей кольорометричної поведінки імпрегнованих волокнистих хемосорбентів (ІВХС) кислих газів із візуальною ідентифікацією моменту «спрацьовування» динамічної поглинальної ємності (ІВХС-І) при поглинанні діоксиду сірки. Хемосорбенти отримані шляхом просочування волокнистих носіїв водними розчинами N-вмісних органічних основ (Am), до складу яких додавали кислотно-основні індикатори (Ind). У роботі використовували ІВХС-І на основі гексаметилентетраміну (ІВХС-HMTA-І) та поліетиленполіаміну (ІВХС-PEPA-І), а також ІВХС-MEA-EDTA-І на основі моноетаноламіну (MEA) та дифенілметанових кислот (EDTA). Як кислотно-основні індикатори було використано наступні: азолітмін, алізарин (AL), лакмоз, метиловий оранжевий, метиловий червоний, Тропеолін О, Тропеолін ОО (TrOO), Тропеолін ООО (TrOOO), конго червоний, бромкрезоловий зелений (BCG), бромкрезоловий пурпуровий (BCP), бромфеноловий синій (BPB), бромфеноловий червоний (BPR), киселиновий червоний (CrR), киселиновий оранжевий, киселиновий синій та феноловий червоний. Виявлено специфіку зміни кольорометричних функцій ІВХС-І під час поглинання ними SO2. Встановлено що забарвлення вихідних зразків ІВХС-І суттєво залежить не лише від будови Ind, а й природи Am, що входять до їхнього складу. Забарвлення зразків на основі лише PEPA (Ind = TrOO, TrOOO, BCG, BCP, BXB, BPB, BPR та CrR) та деяких MEA (Ind = BXB) і HMTA (Ind = AL, BXV) подібне до забарвлення водних розчинів лугів. Відмінність забарвлення решти зразків від забарвлення водних розчинів лугів з одними й тими ж Ind спричинена специфічними взаємодіями між амонійними катіонами та амонійними формами барвників. Забарвлення «спрацьованих» зразків ІВХС-І, як і ІВХС-PEPA-І та ІВХС-HMTA-І, по SO2 відмінні від таких же властивостей водних розчинів бренстедовських кислот. Зміна забарвлення зразків ІВХС-MEA-EDTA-І з трифенілметановими барвниками протікає за бренстедівським механізмом, азо-індикаторів – за рахунок окисно-відновних реакцій із сульфітними сполуками. Молекули PEPA та інші амонієві катіони у складі ІВХС-І стабілізують азотрієві індикатори до виділення основних редокс-перетворень.

Ключові слова: кольорометрія, волокнисті хемосорбенти, діоксид сірки, кислотно-основні індикатори.
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