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The Indicator Impregnated Fibrous Chemisorbents of Sulfur Dioxide Based on Sodium, Monoetanolammonium and Polyethylenepolyammonium Citrates

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A colorimetric study of the interaction between impregnated fibrous chemisorbents and a passive indication of "response" (IFCS-I) based on sodium, monoethanolammonium, polyethylene polyammonium citrates, and "monoethanolamine–monoethanolammonium citrate" and "polyethylene polyamine – polyethylene polyammonium citrate" buffer systems, as well as acid-base indicators (Ind), was conducted. It was established that the color of most initial IFCS-I samples differs from that of classic Bronsted bases and depends significantly on both the structure of the acid-base indicators and the nature of the reagents included in these compositions. This dependence is due to specific interactions between citrate anions, ammonium cations, and anionic forms of dyes. The color change of the IFCS-I studied during the chemisorption of SO2 occurs according to the Bronsted mechanism. Citrate ions act as inhibitors of the redox interaction of S(IV) oxyanions with azoindicators. It is recommended that, in the manufacture of respiratory gas filters, IFCS-I based on monoethanolammonium citrate (Ind = Tropaeolin OOO and Phenyl Red) be used. The determined regularities allow for the prediction of the colorimetric behavior of chemisorbents (based on citrate salts and buffer mixtures) of sulfur dioxide with a passive indication of the absorption capacity "response" moment, which is planned for future use in developing acidic gas chemisorbents with "response" active indication.

Keywords: colorimetry, impregnated fibrous chemisorbents, sulfur dioxide, acid-base indicators

Індикаторні імпрегновані волокнисті хемосорбенти діоксиду сірки на основі цитратів натрію, моноетаноламонію та поліетиленполіамонію

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Проведено колориметричне дослідження взаємодії імпрегнованих волокнистих хемосорбентів зпасивною індикацією "спрацьовування" (IFCS-I) на основі цитратів натрію, моноетаноламонію та поліетиленполіамонію, а також буферних систем "моноетаноламін – цитрат моноетаноламонію" та "поліетиленполіамін – цитрат поліетиленполіамонію" та кислотно-основних індикаторів (Ind). Встановлено, що забарвлення більшості вихідних зразків IFCS-I відмінне від забарвлення класичних бренстедівськихоснов і суттєво залежить як від будови кислотно-основних індикаторів, такі від природи реагентів, що входять до їх складу. Це зумовлено специфічними взаємодіями між аніонами цитрат-аніонами, амонійними катіонами та аніонними формами барвників. Зміна забарвлення досліджених IFCS-I під час хемосорбції SO_2 перебігає за бренстедівським механізмом. Цитрат іони виступають як інгібітори окисно-відновної взаємодії S(IV)оксианіонів із азоіндикаторами. Показано, що при виготовлені протигазових фільтрів респіраторного призначення рекомендується використовувати IFCS-I на основі цитрату моноетаноламонію (Ind = Тропеолін ООО та Феніловий Червоний). Встановлені закономірності дозволяють прогнозувати колориметричну поведінку хемосорбентів (на основі цитратних солей та буферних сумішей) діоксиду сірки з пасивною індикацією моменту "спрацьовування" поглинальної ємності, що планується використовувати в подальшому при розробці хемосорбентів кислих газів з активною індикацією "спрацьовування".

Ключові слова: колориметрія, імпрегновані волокнисті хемосорбенти, діоксид сірки, кислотно-основні індикатори

Introduction

One of the current pressing challenges for manufacturers of personal respiratory protective equipment is the development and integration of sensors to indicate the end-of-life service (ELS) of gas filters [1–3]. Among the most accessible and cost-effective methods for ELS detection is the visual indication of a color change in the indicator layer [2,4–9].

Previously, we developed impregnated fibrous chemisorbents (IFCS) for acidic gases, particularly sulfur dioxide (SO_2), intended for use in respirators with passive ELS indication [7–9]. These chemisorbents were produced by impregnating fibrous carriers (FC) with aqueous solutions of nitrogen-containing organic bases (Am), such as monoethanolamine (MEA), hexamethylenetetramine (HMTA), and polyethylene polyamine (PEPA), in combination with acid-base indicators (Ind). To prevent the loss of volatile amines (e.g., MEA) from the IFCS surface under gas-air mixture (GAM) flow, polybasic organic acids such as citric acid (H_3Cit) were added to the impregnation solutions [9]. This modification improved the protective properties of the IFCS toward SO_2.

Colorimetric methods, particularly visual detection, are widely employed for SO_2 monitoring in air and food products [8–12]. In support of developing indicator-based chemisorbents for acidic and basic gases, our earlier studies examined the behavior and colorimetric properties of acid-base indicators in aqueous solutions [13,14] and on IFCS surfaces [7,8] during interactions with SO_2 or NH_3. The identified patterns in the colorimetric responses of IFCS-I during SO_2 and NH_3 chemisorption enabled us to propose a mechanism for the observed color changes [7,8].

However, to date, no published data are available regarding the behavior of IFCS-I based on aqueous solutions of amines combined with citric acid (H3Cit) in response to SO_2 exposure. Therefore, it is relevant to investigate the colorimetric behavior of IFCS-I systems with visual indication of the dynamic absorption capacity “response” point, specifically those based on sodium citrate (IFCS-Na3Cit-I), monoethanolammonium citrate (IFCS-(MEAH)3Cit-I), and polyethylene polyammonium citrate (IFCS-(PEPAH)3Cit-I), during the chemisorption of sulfur dioxide.

The aim of this work is to determine the specific features of the colorimetric behavior of IFCS-I based on sodium, monoethanolammonium, and polyethylene polyammonium citrates in response to SO_2 chemisorption, with a focus on identifying the moment of dynamic saturation as indicated by a visible color change.

Experimental part

Materials

The following reagents were used without additional purification: chemically pure monoethanolamine (MEA), trisodium citrate (Na_3Cit), and polyethylene polyamine (PEPA, CAS 29320-38-5). A series of acid-base indicators (Ind), with their characteristics summarized in Table S1, were also used. The acid-base characteristics (ABC) of each indicator were described by the pH values of the lower (pH_1) and upper (pH_2) transition boundaries, as well as the pKa values of the functional groups.

As the fibrous carrier (FC), a non-woven needle-punched filter cloth made of Mylar fiber was employed. The material had a thickness of 4.0 mm and a surface density of 400 g/m².

Preparation of chemisorbents

IFCS-Na_3Cit-I. 30 mL of an aqueous solution containing 3.0 mol/L sodium citrate (pH = 8.10) was placed in a 100 mL volumetric flask. 0.04 g of Ind was dissolved according to the recommendations [15] and brought up to the mark with distilled water. The FC was impregnated with the obtained solutions at a rate of 6 mL of solution per FC with a diameter of 58 mm, until complete absorption. The samples were air dried at 20-25 ^{0}C.

IFCS-$(MEAH)_3$Cit-I, IFCS-$(PEPAH)_3$Cit-I. 30 mL of an aqueous solution containing 1.0 mol/L citric acid and 3.0 mol/L MEA (pH = 8.10) or PEPA (pH = 5.45) was placed in a volumetric flask (100 mL). Further procedures were performed similarly to IFCS-Na_3Cit-I.

IFCS-3MEA-$(MEAH)_3$Cit-I and IFCS-3PEPA-$(PEPAH)_3$Cit-I. 30 mL of a buffer solution containing 0.5 mol/l H_3Cit and 3.0 mol/l MEA (pH = 8.10) or PEPA (pH = 5.45) was placed in a volumetric flask (100 ml). The further procedures were performed as described above.

Experimental conditions

Dynamic testing was performed using a specialized gas-dynamic setup as described in [7]. The concentration of SO_2 in the gas-air mixture (GAM) was monitored using an electrochemical gas analyzer (667 EKh 10, Ukranalyt LLC). The IFCS-I samples were tested under simulated respirator operating conditions: SO_2 concentration in the GAM was 150 mg/m³ (15 times the threshold limit value, TLV), relative humidity was 90–95%, and the GAM flow rate was maintained at 1.0 m/s. Breakthrough was defined as the appearance of SO_2 behind the chemisorbent layer at concentrations between 1–3 mg/m³ (TLV = 10 mg/m³).

Colorimetric analysis

The color properties of the IFCS-I samples, both initial and after exposure to SO_2 (“responded”), were assessed using chemical colorimetry [7,8]. The following colorimetric functions (*CF*) were recorded: RGB values; XYZ coordinates (CIEXYZ system); L, A, B coordinates (CIELAB system); color saturation (*S*); hue (*T*); total color difference (ΔE_{76}); yellowness (*G*); relative whiteness (*W*); and intensity of yellow hue (*Ky*).

Analytical signals of the IFCS-I “response” included effective absorption in the red (A_R), green (A_G), and blue (A_B) channels, total absorption (A_T),

color ratio (C_R), and vector length in RGB space (A_V), as calculated according to [7,8]. Color and RGB colorimetric characteristics for the initial and "responded" IFCS-I samples are provided in Tables 1, S2 and S3.

Repeatability and reproducibility were evaluated based on relative standard deviation (RSD), using the principle of variance components and at least three parallel measurements per sample (initial and "responded"), with results presented in Tables S4, S5.

Results and discussion

According to the data presented in Tables 1 and S2, the color of the initial IFCS-I samples depends not only on the molecular structure of the acid-base indicator but also on the chemical nature of the reagents used in their preparation. The presence of sodium citrate and monoethanolammonium in the initial IFCS-I samples imparts a weakly basic character to the surface (pH of impregnation solutions = 8.10), as described in references [22, 23], via the equilibrium 1.

In contrast, the surface of IFCS-I prepared with polyethylenepolyammonium citrate exhibits a mildly acidic environment. A more detailed analysis of the acid-base behavior of sodium, monoethanolammonium, and polyethylenepolyammonium citrates in aqueous solutions is provided in [22, 23].

For IFCS-I samples based on the monoethanolamine–monoethanolammonium citrate (3MEA–$(MEAH)_3$Cit) and polyethylenepolyamine–polyethylenepolyammonium citrate (3PEPA–$(PEPAH)_3$Cit) buffer systems, the surface exhibits stronger alkalinity, with pH values of 10.13 and 8.35, respectively. This is attributed to the following equilibria in addition to equation 2-3.

This interaction leads to color development. However, the colors of the samples based on TrOO (Na_3Cit, $(MEAH)_3$Cit, 3MEA–$(MEAH)_3$Cit, 3PEPA–$(PEPAH)_3$Cit), MR (3MEA–$(MEAH)_3$Cit, 3PEPA–$(PEPAH)_3$Cit), and BXB (3MEA–$(MEAH)_3$Cit, 3PEPA–$(PEPAH)_3$Cit) closely resemble those of the corresponding Brønsted base aqueous solutions with the same indicator (as shown in Tables 1, S2 and S3). In contrast, the observed deviations in color for the other samples are likely due to specific interactions between citrate anions, ammonium cations, and the anionic forms of the dyes.

IFCS–Na_3Cit–I

The chemisorption of sulfur dioxide by IFCS-I samples based on sodium citrate occurs via a series of reactions facilitated by the presence of "free" water on the material surface. As established in prior studies [7, 8, 14, 24], the process proceeds through the equilibria 4-8.

For the initial IFCS–Na_3Cit–I samples containing triphenylmethine indicators, the colorimetric functions x_0 and Gp_0 exhibit a direct (symbatic) correlation with the pH_2 values of the indicator's color transition range, while Z_0 shows an inverse (antibatic) relationship, as described by equation 9. The corresponding parameters are presented in Table S3.

Additionally, the color differences ΔK_Y and ΔW correlate symbatically with the pK_4–*OH* values of the indicators, while the changes in A_G, A_T and C_R demonstrate antibatic dependencies (Table S3).

Upon visual inspection, nearly all IFCS–Na_3Cit–I samples do not exhibit noticeable color change upon exposure to SO_2 ("response" moment), as shown in Table 1. This behavior can be explained by the high proton affinity of citrate anions, which preferentially accept H_3O^+ ions according to the equilibrium 10-11. However, colorimetry enables the detection of subtle color changes that are not discernible to the naked eye (Tables 1, S2 and S3). The colors of the "responded" IFCS–Na_3Cit–I samples (Table 1) differ significantly from those of aqueous solutions of Brønsted acids containing the same indicators (Table S1). Notably, in the case of triphenylmethane-based indicators, the colorimetric functions x_r and Gp_r exhibit a direct (symbatic) correlation with the pH_r values of the indicators' color transition range (Table S6, entries 4 and 5).

$$HOC_3H_4(COO^-)_3 + H_2O \rightleftarrows HOC_3H_4(COOH)(COO^-)_2 + OH^- \quad (1)$$

$$NH_2CH_2CH_2OH + H_2O \rightleftarrows \overset{+}{N}H_3CH_2CH_2OH + OH^- \quad (2)$$

$$NH_2(CH_2CH_2NH)_{k-1}H + k\,H_2O \rightleftarrows \overset{+}{N}H_3(CH_2CH_2\overset{+}{N}H_2)_{k-1}H + k\,OH^- \quad (3)$$

$$SO_2^g \rightleftarrows SO_2^l \quad (4)$$

$$SO_2^l + nH_2O \rightleftarrows SO_2\cdot H_2O + (n\text{-}1)\,H_2O \quad (5)$$

$$SO_2\cdot H_2O + OH^- \rightarrow SO_3^{2-} + 2H_2O \quad (6)$$

$$SO_2\cdot H_2O + SO_3^{2-} \rightleftarrows 2HSO_3^- \quad (7)$$

$$2HSO_3^- \rightleftarrows S_2O_5^{2-} + H_2O \quad (8)$$

Table 1. Color of samples IFCS-I.

Reagent	Na_3Cit		$(MEAH)_3Cit$		3MEA-$(MEAH)_3Cit$		$(PEPAH)_3Cit$		3PEPA-$(PEPAH)_3Cit$	
Ind	Initial	"Responded"	Initial	"Responded"	Initial	"Responded"	Initial	"Responded"	Initial	"Responded"
Az										
LA	-									
MR										
TrO										
TrOO										
TrOOO										
CoR										
BCG	-									
BXB										
BPB										
XO	-									
PR										

The observed dependencies (Table S6; entries 4–12) indicate that the color change on the surface of IFCS–Na_3Cit–I samples containing the specified indicators during SO_2 chemisorption occurs via a Brønsted-type mechanism, operating in a weakly acidic environment—similar to that observed for IFCS–MEA–EDTA–I systems [7]. For azo indicators of the tropaeolin series, additional correlations were identified (Table S6; entries 13–27). Specifically, an increase in the pH_1 value of the tested indicators corresponds to a greater change in the yellow hue intensity (ΔK_Y) of the IFCS–Na_3Cit–I samples upon "response" to SO_2 (Table S6, entry 28).

A direct (symbatic) correlation is observed between the colorimetric functions B, X, Y, Z, S, and T of the "responded" IFCS–Na_3Cit–I samples and the corresponding functions of the initial samples. This relationship is described by equation 12, with the fitting parameters presented in Table S7.

IFCS–(MEAH)$_3$Cit–I

The chemisorption of SO_2 by IFCS–$(MEAH)_3$Cit–I samples proceeds via a series of reactions, specifically reactions 4–8 and 13–15.

For the triphenylmethine indicator series, BPB (4.0) < BCG (4.6) < XO (6.4) < BXB (6.8) < PR (8.4), a symbatic increase is observed in both the pK_4–*OH* values and the colorimetric functions, R, X_0, Y_0, x_0, z_0, L_0, T_0, K_{Y0}, and Gp_0 of the initial IFCS–$(MEAH)_3$Cit–I samples, in accordance with Equation (9); the corresponding parameters are listed in Table S8 (entries 1–9). Additionally, a direct correlation is observed between the values of Y_0 and pH_2 for these IFCS samples (Table S8, entry 10).

In the case of IFCS-I samples based on monoethanolammonium citrate (excluding the BXB-based sample), in contrast to those based on Na_3Cit, it is possible to visually observe the "response" moment to SO_2 exposure. This effect is likely due to hydrogen bonding between MEA-derived ammonium cations and citrate anions, which inhibits the progression of reaction 10 while facilitating reaction 11 [23]. As a result, indicators with a color transition range from pH 1.3 to 12.7, when incorporated into IFCS–$(MEAH)_3$Cit–I compositions, enable clear visual detection of SO_2 chemisorption.

For the "responded" IFCS–$(MEAH)_3$Cit–I samples containing triphenylmethine indicators, direct (symbatic) dependencies are observed between the colorimetric functions R_r, X_r, Y_r, x_r, z_r, L_r, b_r, T_r, K_{Yr}, Gp_r, W_r, ΔW, and A_R and the $pK_{4\text{-}OH}$ values of the indicators, as described by equation 9; the corresponding parameters are listed in Table S6 (entries 1–23).

In contrast, for the initial IFCS–$(MEAH)_3$Cit–I samples containing azo indicators, only a single correlation was identified (Table S6, entry 24), suggesting the presence of specific interactions within the $NH_2CH_2CH_2OH$ – $HOC_3H_4(COOH)_3$ – Ind – H_2O system. These interactions likely involve the formation of ionic associates or ion–molecular complexes, consistent with the mechanisms proposed in [23, 25].

For the "responded" azo-based IFCS–$(MEAH)_3$Cit–I samples, an inverse (antibatic) relationship is observed between pH_1 values and the whiteness function W_r, while a direct (symbatic) dependence exists between pH_1 and the change in yellow hue intensity (ΔK_Y), as shown in Table S6 (entries 25 and 26).

During SO_2 chemisorption by IFCS–$(MEAH)_3$Cit–I samples containing azo indicators, the observed color change of the surface appears to result primarily from acid–base dissociation processes. This is supported by the presence of symbatic dependencies between the colorimetric functions of the initial and "responded" samples, distinguishing them from IFCS–MEA–EDTA–I systems [7], where redox reactions between sulfur(IV) oxyanions and azo indicators dominate. The described correlations are mathematically represented by equation 12, with regression parameters summarized in Table S9.

$$CF_i = A_i + B_i \cdot \mathrm{ABC} \quad (9)$$

$$HOC_3H_4(COO^-)_3 + H_3O^+ \rightleftarrows HOC_3H_4(COOH)(COO^-)_2 \quad (10)$$

$$Ind^{2-} + H_3O^+ \rightleftarrows HInd^- \quad (11)$$

$$CF_r = A_i + B_i \cdot CF_0 \quad (12)$$

$$2\,\{\overset{+}{N}H_3CH_2CH_2OH\}_3\{HOC_3H_4(COO^-)_3\} + SO_2\cdot H_2O \rightarrow \quad (13)$$

$$\rightarrow 2\,\{\overset{+}{N}H_3CH_2CH_2OH\}_2\{HOC_3H_4(COOH)(COO^-)_2\} + \{\overset{+}{N}H_3CH_2CH_2OH\}_2(HSO_3^-)$$

$$SO_2\cdot H_2O + \{\overset{+}{N}H_3CH_2CH_2OH\}_2(SO_3^{2-}) \rightleftarrows \{\overset{+}{N}H_3CH_2CH_2OH\}_2(HSO_3^-) \quad (14)$$

$$2\{\overset{+}{N}H_3CH_2CH_2OH\}_2(HSO_3^-) \rightleftarrows \{\overset{+}{N}H_3CH_2CH_2OH\}_2(S_2O_5^{2-}) + H_2O \quad (15)$$

$$CF(\text{IFCS-3PEPA-(PEPAH)}_3\text{Cit-I}) = A_i + B_i \cdot CF(\text{IFCS(PEPAH)}_3\text{Cit-I}) \quad (16)$$

IFCS–3MEA–(MEAH)$_3$Cit–I

For IFCS–3MEA–(MEAH)$_3$Cit–I samples containing triphenylmethine indicators, several correlations are observed and can be described by equation 9; the corresponding parameters are provided in Table S10. In the case of azo indicators incorporated into IFCS-I formulations based on the "monoethanolamine–monoethanolammonium citrate" buffer system, a greater number of dependencies are observed (Table S11, entries 7–20) compared to those based solely on monoethanolammonium citrate (Table S9, entry 1).

The addition of 3MEA to the composition of IFCS–(MEAH)$_3$Cit–I leads to a slight increase in the surface basicity, as previously noted. As a result, the "response" to SO_2 can also be visually detected when using BXB as the indicator. However, the color transition range of BXB becomes narrower, limited to pH 3.0–10.4, which still allows for effective visual detection of the end-of-service life (ELS) in the presence of SO_2. In contrast, indicators such as TrO and TrOO do not enable visual detection under these conditions. The Brønsted-type mechanism governing the color change of IFCS–3MEA–(MEAH)$_3$Cit–I during SO_2 chemisorption is further supported by the observed regularities, which are described by equation 12; the corresponding parameters are listed in Table S11.

IFCS-(PEPAH)$_3$Cit-I

TrOOO and BCG, when incorporated into IFCS-I based on (PEPAH)$_3$Cit, enable visual detection of the end-of-service life (ELS) in response to SO_2 exposure (Table 1), in contrast to IFCS–Na$_3$Cit–I systems. This occurs despite the fact that the pH of the impregnation solutions in the former case is lower than in the latter.

For triphenylmethine indicators incorporated into IFCS-I based on polyethylene polyammonium citrate, multiple dependencies of the colorimetric functions were identified for the initial samples, "responded" samples, and analytical "response" signals. These relationships are described by equation 9; the corresponding parameters are provided in Table S12 (entries 1–6 for initial samples, 7–11 for "responded" samples, and 12–16 for analytical response signals).

In the case of monoazo indicators within the IFCS–(PEPAH)$_3$Cit–I composition, similar equation 9-type dependencies were also observed (Table S12, entries 17–19). Moreover, for all investigated indicators in IFCS formulations based on (PEPAH)$_3$Cit, Equation (12)-type relationships were established (see Table S13), further confirming that the colorimetric "response" to SO_2 proceeds via a Brønsted acid-base mechanism.

IFCS–3PEPA–(PEPAH)$_3$Cit–I

The incorporation of PEPA into the composition of IFCS–(PEPAH)$_3$Cit–I enables the use of a broader range of indicators (pH_1–pH_2 = 3.0–10.4) for effective visual detection of the end-of-service life (ELS) in response to SO_2 exposure. The dependencies observed for IFCS-I based on the polyethylene polyamine–polyethylene polyammonium citrate buffer system are described by equations 9 and 12, with the corresponding parameters listed in Tables S14 and S15, respectively.

For the colorimetric functions of IFCS-I samples based on (PEPAH)$_3$Cit salt and the 3PEPA–(PEPAH)$_3$Cit buffer system, symbatic relationships were found and are described by equation 16, with parameter values provided in Table S16. However, no consistent relationships were observed between the colorimetric functions of the initial and "responded" samples across systems such as IFCS–(MEAH)$_3$Cit–I vs. IFCS–3MEA–(MEAH)$_3$Cit–I or IFCS–(MEAH)$_3$Cit–I vs. IFCS–(PEPAH)$_3$Cit–I.

During the "response" of most IFCS-I samples to sulfur dioxide, surface discoloration is observed (Tables 1, S2 and S3), as indicated by the positive values of ΔW (whiteness increase) and negative values of total absorption (A_T). In line with the methodology proposed in [1], the total absorption (A_T) was selected as the principal analytical "response" signal for quantifying SO_2 chemisorption. The absolute values of A_T vary depending on the indicator and matrix composition, and they tend to decrease progressively across indicator series, reflecting diminishing color intensity upon gas exposure. The A_T values for the studied systems are as follows:

IFCS–Na$_3$Cit–I:
TrOOO (0.001) < MR (–0.002) < AZ (–0.005) < BXB (–0.022) < TrO (0.024) < CoR (0.028) < PR (–0.037) < BPB (0.071) << TrOO (–0.102)

IFCS–(MEAH)$_3$Cit–I:
CoR (0.005) < XO (–0.008) ≈ BXB (–0.011) < AZ (–0.044) < BPB (0.077) ≈ TrO (0.071) < MR (0.093) < TrOO (–0.114) < BCG (–0.270) < LA (0.317) < TrOOO (–0.689) < PR (–0.744)

IFCS–3MEA–(MEAH)$_3$Cit–I:
TrO (–0.019) < TrOOO (–0.063) < TrOO (0.072) < CoR (0.084) < XO (0.099) < BPB (–0.103) < LA (–0.115) < PR (0.140) < MR (–0.159) < AZ (–0.163) < BXB (–0.316) < BCG (–0.597)

IFCS–(PEPAH)$_3$Cit–I:
LA (–0.017) < XO (–0.018) < TrOO (–0.024) < AZ (–0.042) < MR (–0.053) < BXB (0.108) < CoR (0.160) < TrO (–0.208) < BPB (–0.211) < BCG (0.303) < PR (–0.324) < TrOOO (0.360)

IFCS–3PEPA–(PEPAH)$_3$Cit–I:
BCG (–0.005) < TrOO (–0.015) < BPB (–0.025) ≈ XO (–0.026) < AZ (0.042) < MR (–0.066) < LA (–0.086) < BXB (0.108) < CoR (0.181) < PR (–0.326) < TrOOO (–0.371) < TrO (–0.656).

Therefore, based on the obtained total absorption data for the investigated IFCS-I systems, it is recommended to employ IFCS–I formulations based on monoethanolammonium citrate ((MEAH)$_3$Cit) in combination with Tropaeolin OOO or Phenol Red as indicators for the production of gas filters intended for respirators.

Conclusions

Based on chemical colorimetry data, the specific acid-base behavior of impregnated fibrous chemisorbents (IFCS-I) based on citrate salts and their buffer systems was elucidated, demonstrating a detectable response to sulfur dioxide. It was found that the initial color of most IFCS-I samples differs from that of classical Brønsted bases and is strongly influenced not only by the molecular structure of the acid-base indicators but also by the chemical nature of the components within the chemisorbent system. This behavior is attributed to specific interactions between citrate anions [$HOC_3H_4(COO^-)_3$], ammonium cations, and the anionic forms of the dyes.

Due to competitive interactions with H^+ ions, citrate anions inhibit the binding of protons to the anionic forms of acid-base indicators with wide color transition ranges (pH_1–pH_2 = 1.3–12.7). As a result, IFCS–Na_3Cit–I samples do not enable visual detection of the "response" moment upon exposure to sulfur dioxide. In contrast, monoethanolammonium cations form hydrogen-bonded associates with citrate anions [$HOC_3H_4(COO^-)_3$], which promote a visual response to SO_2 in the presence of most indicators with similar pH ranges (excluding BXB). Although BXB can function in IFCS-I based on the monoethanolamine–monoethanolammonium citrate buffer system, the effective pH range for ELS indication is narrowed to 3.0–10.4.

The incorporation of polyethanolammonium citrate in IFCS-I creates a weakly acidic surface environment (pH ≈ 5.45). Nevertheless, indicators such as LA, Tropaeolin OOO (TrOOO), and BCG in IFCS–$(PEPAH)_3$Cit–I allow reliable visual detection of the end-of-service life (ELS) under SO_2 exposure. Furthermore, the addition of PEPA to IFCS–$(PEPAH)_3$Cit–I formulations expand the applicable indicator pH range (pH_1–pH_2 = 3.0–10.4), enhancing the flexibility for "response" detection.

The observed color changes in IFCS–I based on sodium, monoethanolammonium, and polyethylene polyammonium citrates, as well as in their respective buffer systems with monoethanolamine or polyethyleneamine, occur via Brønsted acid-base interactions. Citrate ions serve as inhibitors of redox reactions between S(IV) oxyanions and azo indicators.

Based on a comprehensive analysis of the colorimetric behavior of acid-base indicators in SO_2-sensitive chemisorbents, we recommend the use of IFCS-I based on monoethanolammonium citrate in combination with Tropaeolin OOO or Phenyl Red for manufacturing gas filters with visual ELS indication.

The established correlations provide a basis for predicting the colorimetric behavior of citrate-based chemisorbents in the removal of sulfur dioxide. These findings can be applied to the future development of acid gas chemisorbents equipped with active visual response indicators, offering practical solutions for both passive and active monitoring of filter exhaustion.

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