

OIL SHALE RESORCINOLS – EFFECTIVE REAGENTS FOR NITRITE. AN ALGORITHM FOR THE INFLUENCE OF pH ON OPTICAL DENSITY

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The theoretical basis is presented for testing nitrite with alkylresorcinols, the main water-soluble phenolic compounds of oil shale origin. An algorithm is deduced to describe the joint effect of pH and concentration of the reagents on the optical density (E). Acidic dissociation of the nitrosation products of 5-methylresorcinol and of the cobalt and iron (II) nitroso-5-methyl resorcinolate complexes is studied. Formation of a colloidal suspension is considered. The effect of pH on the contributions to E of the five coloured species formed is described. Acidic dissociation constants, molar extinction coefficients, stability constants, and solubility products of the species formed are estimated.

Introduction

Recently a new test method was presented [1] for photometric estimation of nitrite with alkylresorcinols, the main water-soluble phenolic compounds of oil shale origin. An algorithm was deduced [2] to describe the concentration effect of the reagents applied for formation of the coloured nitrosoalkylresorcinolate complex (MeA_n). In the paper [2] the stability of MeA_n was expressed by means of the optical density measured (E) and the initial concentrations of nitrite (C_N) and the cation applied (C_{Me}) as follows:

$$\beta_H = (E/\epsilon_H) / \{ C_{\text{Me}}(C_N - nE/\epsilon_H)^n \} \quad (1)$$

where β_H was the apparent stability constant, and ϵ_H was the apparent molar extinction coefficient, both valid at the optimum pH only ($\text{pH}_{\text{Co}} = 4.0$, $\text{pH}_{\text{Fe}} = 3.3$). The value of n was 3 for cobalt complexes and 2 for iron com-

plexes. The unknown values of β_H and ϵ_H were found from the coefficients of the linear relationship between $(E/C_{Me})^{1/n}$ and E when the main oil shale originated phenols, 5-methylresorcinol (5-MR) or 2,5-dimethylresorcinol (2,5-DMR), and cobalt or iron(II) sulphate were applied as reagents. A twice higher sensitivity was found for the cobalt complexes formed with 5-MR compared with 2,5-DMR.

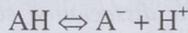
In this work, the essence of the joint effect of pH and concentrations of the reagents on the optical density was studied. To solve the problem, an algorithm for the prediction of E was deduced where the acidic dissociation of both nitrosoalkylresorcinol and the complex, as well as the complex stability and solubility were considered. The effect of pH on the partial contributions to the E values of the five coloured species formed were described. The characteristic constants of the participating equilibrium reactions were estimated using the most promising reagents established in [1], 5-MR as alkylresorcinol, and iron(II) and cobalt cations as Me.

Theoretical Approach

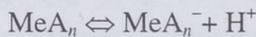
Relationship between E , C_N , C_{Me} and pH in Solutions of MeA_n

Equation (1) assumes that the equilibrium concentration of the complex formed depends on the total concentration of nitrosoalkylresorcinol remained after the complex formation.

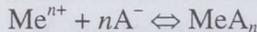
Actually, both nitrosoalkylresorcinol and the complex, as weak acids, can occur in two forms of coloured species:



and



According to the complex formation reaction



the complex is in equilibrium with the anionic species (A^-) only. To describe the effect of pH on E , Equation (1) should be modified taking into account the dissociation percentages and contributions of the coloured species formed. The dissociation coefficients K_1 and K_2 are expressed as follows

$$K_1 = x_2[H^+]/x_1 \quad (2)$$

$$K_2 = x_4[H^+]/x_3 \quad (3)$$

where x_1 , x_2 , x_3 and x_4 represent the equilibrium concentrations of AH, A^- , MeA_n and MeA_n^- , respectively.

According to the nitrite test-method proposed in [1], C_{Me} should be some orders higher than C_N . Then the approximation

$$[Me] = C_{Me} \quad (4)$$

can be applied.

When, thanks to the prescribed excess of alkylresorcinol, practically all nitrite is applied for nitrosation, the mass balance of nitrite, the stability constant of the complex (β) and the optical density measured are compiled as follows:

$$C_N = x_1 + x_2 + nx_3 + nx_4 \quad (5)$$

$$\beta = (x_3 + x_4)/(C_{Me}x_2^n) \quad (6)$$

$$E = \varepsilon_1x_1 + \varepsilon_2x_2 + \varepsilon_3x_3 + \varepsilon_4x_4 \quad (7)$$

where ε with indexes 1–4 represent the molar extinction coefficients of the corresponding species.

Algorithm for Estimation of β and ε_3

Equation (6) gives for the total concentration of the complex the expression

$$x_3 + x_4 = \beta C_{Me}x_2^n \quad (8)$$

According to Equations (2)–(5), the concentrations of the other coloured species formed can be related with the total concentration of the complex as follows

$$x_4 = K_2(x_3 + x_4)/(K_2 + [H^+]) \quad (9)$$

$$x_3 = x_4[H^+]/K_2 \quad (10)$$

$$x_2 = K_1[C_N - n(x_3 + x_4)]/(K_1 + [H^+]) \quad (11)$$

$$x_1 = [H^+][C_N - n(x_3 + x_4)]/(K_1 + [H^+]) \quad (12)$$

Substitution of Equations (9)–(12) into Equation (7) and replacements give for the total concentration of the complex the pH-dependence

$$x_3 + x_4 = (K_2 + [H^+])[E(K_1 + [H^+]) - C_M(\varepsilon_1[H^+] + \varepsilon_2K_1)]/[\varepsilon_3(K_1 + [H^+])(qK_2 + [H^+]) - n(\varepsilon_1[H^+] + \varepsilon_2K_1)(K_2 + [H^+])] \quad (13)$$

where the ratio of the molar extinction coefficients

$$q = \varepsilon_4/\varepsilon_3 \quad (14)$$

was applied because the direct estimation of ε_4 and ε_3 was unrealisable. This problem will be discussed in more detail farther below.

Substitution of Expressions (13) and (11) for $(x_3 + x_4)$ and x_2 in Equation (6) and replacements result the algorithm for the stability constant

$$\beta = (K_2 + [H^+])[E(K_1 + [H^+]) - C_N(\varepsilon_1[H^+] + \varepsilon_2K_1)]/[\varepsilon_3(K_1 + [H^+])(qK_2 + [H^+]) - n(\varepsilon_1[H^+] + \varepsilon_2K_1)(K_2 + [H^+])]/\{K_1[C_N - n(x_3 + x_4)]/(K_1 + [H^+])\}^n/C_{Me} \quad (15)$$

The unknown values of the constants β and ε_3 can be computed from Equation (15) by the least squares method. The values of K_1 , K_2 , ε_1 , ε_2 , and q should be known before. Estimation of these constants by special series of experiments will be described later.

Algorithm for Prediction of E

When all the constants have been found, the optical density of the solution at any pH can be predicted using the algorithm

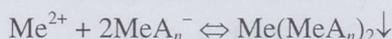
$$E = \varepsilon_1[H^+][C_N - n(x_3 + x_4)]/(K_1 + [H^+]) + \varepsilon_2K_1[C_N - n(x_3 + x_4)]/[(K_1 + [H^+]) + \varepsilon_3(x_3 + x_4)[H^+]/(K_2 + [H^+]) + q\varepsilon_3K_2(x_3 + x_4)/(K_2 + [H^+])] \quad (16)$$

where $(x_3 + x_4)$ should be calculated from Equation (13).

It is noteworthy that a turbidity can arise in the solutions of the complexes near the optimum pH. In such cases Equation (16) is not valid. Next, an approach for modelling of the turbid solutions will be discussed.

Relationship between E , C_N , C_{Me} and pH in Turbid Solutions

The arising turbidity can be explained by the reaction between cations and anionic species of the complex whose amount increases with increasing pH:



The solubility product of the precipitate (P) is expressed by the equation

$$P = C_{Co}x_4^2 \quad (17)$$

Consequently, concentration of the anionic species of the complex should be constant in turbid solutions and is fixed by the cation concentration as follows:

$$x_4 = (P/C_{Co})^{1/2} \quad (18)$$

Concentrations of the other coloured species depend on pH and are determined by the characteristic coefficients and by the unchangeable under the test conditions values of x_4 and C_{Me} as follows:

$$x_3 = x_4[H^+]/K_2 \quad (19)$$

$$x_3 + x_4 = x_4(K_2 + [H^+])/K_2 \quad (20)$$

$$x_2 = [x_4(K_2 + [H^+])/(K_2C_{Me}\beta)]^{1/n} \quad (21)$$

$$x_1 = [x_4(K_2 + [H^+])/(K_2C_{Me}\beta)]^{1/n}[H^+]/K_1 \quad (22)$$

When, thanks to a sufficient excess of alkylresorcinol, practically all nitrite is applied for nitrosation, the mass balance of nitrite is expressed as

$$C_N = x_1 + x_2 + nx_3 + nx_4 + 2nx_5 \quad (23)$$

where x_5 is the molar concentration of the indissoluble species in the bulk of solution.

Equation (23) gives for the concentration of the indissoluble species the expression

$$x_5 = (C_N - x_1 - x_2 - nx_3 - nx_4)/2n \quad (24)$$

Alike Equation (7), the optical density of turbid solutions is compiled from the partial extinctions of the coloured species

$$E = \varepsilon_1x_1 + \varepsilon_2x_2 + \varepsilon_3x_3 + \varepsilon_4x_4 + \varepsilon_5x_5 \quad (25)$$

Algorithm for Estimation of P and ε_5

Equations (24) and (25) give for the molar extinction coefficient of the colloidal particles the expression

$$\varepsilon_5 = 2n(E - \varepsilon_1x_1 - \varepsilon_2x_2 - \varepsilon_3x_3 - \varepsilon_4x_4)/(C_N - x_1 - x_2 - nx_3 - nx_4) \quad (26)$$

Substitution of the concentrations in Equation (26) with their expressions in Equations (18), (19), (21), and (22) and (24) gives a relationship which includes two unknown constants, P and ε_5 . The values of the constants can be computed by the least squares method.

Algorithm for Prediction of E in Turbid Solutions

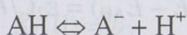
When all the constants have been found, the optical density at any pH in the region of colloidal solutions can be calculated by the algorithm

$$\begin{aligned} E = & \varepsilon_1[H^+][(P/C_{Co})^{1/2}(K_2 + [H^+])/(K_2C_{Me}\beta)]^{1/n}/K_1 + \\ & + \varepsilon_2\{(P/C_{Co})^{1/2}(K_2 + [H^+])/(K_2C_{Me}\beta)\}^{1/n} + \varepsilon_3(P/C_{Co})^{1/2}[H^+]/K_2 + \varepsilon_4(P/C_{Co})^{1/2} + \\ & + \varepsilon_5\{(C_N - [H^+][(P/C_{Co})^{1/2}(K_2 + [H^+])/(K_2C_{Me}\beta)]^{1/n}/K_1 - [(P/C_{Co})^{1/2}(K_2 + \\ & + [H^+])/(K_2C_{Me}\beta)]^{1/n} - n(P/C_{Co})^{1/2}[H^+]/K_2 - n(P/C_{Co})^{1/2}\}/2n \end{aligned} \quad (27)$$

Algorithms for Estimation of K_1 , K_2 , ε_1 , ε_2 , and $\varepsilon_4/\varepsilon_3$

Dissociation characteristics of any coloured reagent can be easily found from a series of extinction values estimated at various pH values.

For any acidic dissociation



the dissociation coefficient, the mass balance of the species, and the optical density measured are described by the formulas

$$K = [A^-][H^+]/[AH] \quad (28)$$

$$C = [AH] + [A^-] \quad (29)$$

$$E = \varepsilon_1[AH] + \varepsilon_2[A^-] \quad (30)$$

Approach I

When an acidic dissociation is practically completed at higher values of pH, a steady state of the optical density (E_A) should be obtained. Then the value for ε_2 can be found easily from

$$\varepsilon_2 = E_A/C \quad (31)$$

Combining Equations (28)–(31) gives the auxiliary relationship

$$(E_A - E)/[H^+] = -\varepsilon_1 C/K + E/K \quad (32)$$

which represents a linear regression

$$Y_1 = a_1 + b_1 E \quad (33)$$

of the function

$$Y_1 = (E_A - E)/[H^+] \quad (34)$$

versus optical density measured.

The formulas of the regression coefficients

$$a_1 = -\varepsilon_1 C/K \quad (35)$$

$$b_1 = 1/K \quad (36)$$

allow to calculate the acidic dissociation characteristics from the slope and intercept of the straight line (33) as follows

$$K = 1/b_1 \quad (37)$$

$$\varepsilon_1 = -a_1/(b_1 C) \quad (38)$$

Approach II

When a constant value of the optical density for the molecular form (E_{AH}) is evident at the lower region of pH values, it is easy to calculate the extinction coefficient for AH by

$$\varepsilon_1 = E_{AH}/C \quad (39)$$

Combining Equations (28)–(30) and (39) gives the auxiliary relationship

$$[H^+](E - E_{AH}) = \varepsilon_2 C/K - E/K \quad (40)$$

which represents a linear regression

$$Y_2 = a_2 - b_2E \quad (41)$$

where the function value is calculated by means of the experimental data as follows

$$Y_2 = [H^+](E - E_{AH}) \quad (42)$$

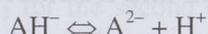
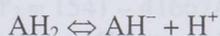
The dissociation characteristics can be found from the plot of Y_2 versus E by analogy to the plot of Y_1 versus E as

$$K = 1/b_2 \quad (43)$$

$$\varepsilon_2 = a_2/(b_2C) \quad (44)$$

Algorithm for Estimation of $K_1(\text{II})$ and $\varepsilon_2(\text{II})$ for Dissociation of Two-Basic Acids

Dissociation of a two-basic acid, AH_2 , involves two consecutive reactions



with dissociation coefficients $K_1(\text{I})$ and $K_1(\text{II})$, and molar extinction coefficients ε_1 , $\varepsilon_2(\text{I})$ and $\varepsilon_2(\text{II})$.

The characteristics of the first dissociation, $K(\text{I})$, ε_1 and $\varepsilon_2(\text{I})$, can be found following *Approach II* under the acidic conditions where the second dissociation is negligible.

Characteristics of the second dissociation can be found as follows.

Co-solution of the relationships

$$K_1(\text{I}) = [\text{AH}^-][\text{H}^+]/[\text{AH}_2] \quad (45)$$

$$K_2(\text{II}) = [\text{A}^{2-}][\text{H}^+]/[\text{AH}^-] \quad (46)$$

$$C = [\text{AH}_2] + [\text{AH}^-] + [\text{A}^{2-}] \quad (47)$$

$$E = \varepsilon_1[\text{AH}_2] + \varepsilon_2(\text{I})[\text{AH}^-] + \varepsilon_2(\text{II})[\text{A}^{2-}] \quad (48)$$

enables to compile a linear regression

$$Y_3 = a_3 - b_3E \quad (49)$$

where

$$Y_3 = [H^+]^2(E - C\varepsilon_1)/K_1(\text{I}) + [H^+](E - C\varepsilon_2(\text{I})) \quad (50)$$

$$a_3 = \varepsilon_2(\text{II})CK_1(\text{II}) \quad (51)$$

$$b_3 = K_1(\text{II}) \quad (52)$$

The characteristics can be found from the coefficients of Regression (49) by analogy to *Approach I* and *Approach II* as follows:

$$K_1(\text{II}) = b_3 \quad (53)$$

$$\varepsilon_2(\text{II}) = a_3/(b_3C) \quad (54)$$

Algorithm for Estimation of K_2 and q for the Complexes

The complex MeA_n obtains characteristics of a moderately weak acid because the electron density distribution in the complex promotes the acidic dissociation of the second OH-group of nitroso-5-MR. To estimate the values for ϵ_3 and ϵ_4 the authentic concentration of the complex in the solution should be known. Unfortunately, concentration of the solution obtained by equilibrium processes of formation, solid-phase extraction and re-extraction is uncertain. So, instead of the absolute value, the ratio $q = \epsilon_4/\epsilon_3$ should be found as the equivalent to the ratio E_A/E_{AH} . When the optical density for the anionic form E_A is known, that for the molecular form E_{AH} as well K_2 can be estimated from the coefficients of the linear relationship (32) where $\epsilon_1 C$ is replaced by E_{AH}

$$(E_A - E)/[\text{H}^+] = -E_{\text{AH}}/K_2 + E/K_2 \quad (55)$$

Experimental, Computation and Discussion

Estimation of K_1 , ϵ_1 , and ϵ_2 for 4-Nitroso-5-Methylresorcinol and 2,4-Dinitroso-5-Methylresorcinol

The reaction products of nitrous acid with 5-MR, 4-nitroso-5-methylresorcinol (AH) and 2,4-dinitroso-5-methylresorcinol (AH_2) are new commercially not obtainable reagents. Therefore, for this work, the reagents were synthesised according to the procedures described in [3].

For estimation of the dissociation characteristics of the nitroso compounds their $2 \times 10^{-4} \text{ M}$ solutions in 0.01M H_2SO_4 , CH_3COOH , CH_3COONa , or NaOH were mixed to obtain series with pH 2–12.

The plots of E (recorded on the SPEKOL 11 at 420 nm in cells 10 mm) versus pH (measured using METLER-TOLEDO 320 pH meter) are depicted in Fig. 1a.

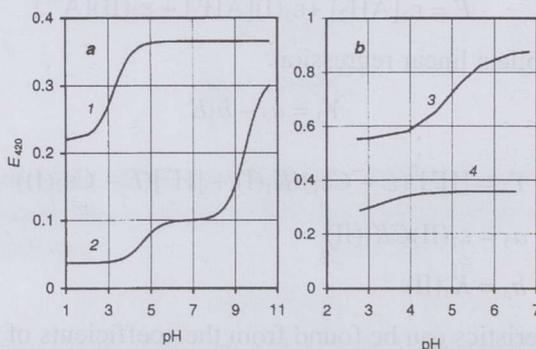


Fig. 1. Plot of optical density versus pH for: a – $2 \times 10^{-4} \text{ M}$ solutions of 4-nitroso-5-methylresorcinol (curve 1) and 2,4-dinitroso-5-methylresorcinol (curve 2); b – eluted concentrate of CoA_3 (curve 1) and FeA_2 (curve 2)

The results give a one-step curve (1) for the mono-nitroso compound with dissociation coefficient K_1 . The practically unchanging optical density, $E_A = 0.365$, is evident for this curve above pH 5–5.5. So, *Approach I* can be applied. The experimental data depicted in Fig. 1a yield for mono-nitroso-5-methylresorcinol the auxiliary function

$$Y_1 = 398 - 1825E \quad (56)$$

A significantly lower two-step curve (2) is evident for the dinitroso-5-methylresorcinol. The steady state of E for the anionic species of the dinitroso compound, A^{2-} , cannot be obtained in the pH region studied. So, in this case, *Approach II* is more appropriate. A practically constant optical density can be fixed for AH_2 between pH 2–2.5. Using this value, $E_{AH} = 0.037$, the auxiliary function (40) for the first dissociation of AH_2 obtains the trend line

$$Y_2 = 1541 - 41667E \quad (57)$$

The auxiliary function Y_3 for the second dissociation (50) depends, according to Equation (49), on E as follows:

$$Y_3 = 1580 - 3.03 \times 10^9 E \quad (58)$$

The dissociation characteristics of the nitroso compounds calculated from Equations (37), (38), (43), (44), (53) and (54) by means of the coefficients in Equations (56)–(58) are presented in Table 1.

Table 1. Dissociation and Molar Extinction Coefficients of 4-Nitroso-5-Methylresorcinol (AH) and 2,4-Dinitroso-5-Methylresorcinol (AH₂)

| | K_1 or $K_1(I)$ | $K_1(II)$ | ϵ_1 | ϵ_2 or $\epsilon_2(I)$ | $\epsilon_2(II)$ |
|-----------------|-------------------|--------------|--------------|---------------------------------|------------------|
| AH | $5.48E - 04$ | – | 1096 | 1827 | – |
| AH ₂ | $2.40E - 05$ | $3.30E - 10$ | 185 | 500 | 1,580 |

Estimation of K_2 and ϵ_4/ϵ_3 for the Complexes

The reagent grade complexes are required to estimate the dissociation characteristics. For this aim CoA_3 and FeA_2 were separated from the excess of the reagents by solid phase disk-extraction on the J. T. Baker *Speedisk* SDB, washed with water and eluted with ethanol. The aliquots of the concentrates obtained were diluted to 1 : 1 with various pH buffer solutions. Thereafter, immediately their optical density was estimated. A notable effect of pH on the optical density of the complexes in Fig. 2 proves that the acidic dissociation of the complexes takes place. The auxiliary curves calculated according to Equation (32) starting from $E_A = 0.88$ for CoA_3 and $E_A = 0.368$ for FeA_2 obtain the trend lines

$$Y_{1_{\text{Co}}} = -50097 + 9091E \quad (59)$$

$$Y_{1_{\text{Fe}}} = -1852 + 501E \quad (60)$$

The dissociation characteristics of the complexes calculated from the coefficients of Regressions (59) and (60) are given in Table 2.

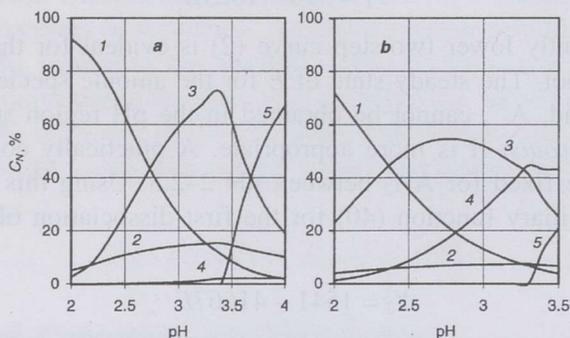


Fig. 2. Effect of pH on the distribution of species at formation of: *a* – CoA_3 ; *b* – of FeA_2 . Curves: 1 – AH; 2 – A^- ; 3 – MeA_n ; 4 – MeA_n^- ; 5 – $\text{Me}(\text{MeA}_n)_2$

Table 2. Characteristics of the Complexes

| | K_2 | q | ϵ_3 | ϵ_4 | ϵ_5 | β | P |
|----------------|------------|-------|--------------|--------------|--------------|------------|------------|
| CoA_3 | $1.10E-05$ | 1.597 | 22,000 | 35,134 | 53,300 | $1.37E+13$ | $2.43E-16$ |
| FeA_2 | $5.40E-04$ | 1.361 | 9,080 | 12,360 | 51,400 | $7.83E+08$ | $2.43E-13$ |

Discussion about the Reaction Products

The mathematical models deduced in the theoretical part of this paper were applied and proved using the experimental data from our previous paper [1]. The first two columns in Table 3 represent the experimental data. At that, the values of optical density measured are reduced to the cell length 1 cm ($E = E_{\text{exp}}/l$).

When pH is 2, the complex formation is negligible. So, the values of the optical density found must represent mainly absorbance of the molecular species of the nitroso compound AH or AH_2 formed. According to Table 1, when C_N is $5 \times 10^{-5} \text{M}$, the E value for the mononitroso compound should be 0.055, and for the dinitroso compound only 0.005. The estimated optical density of the cobalt solution is 0.072 and iron(II) solution 0.099. Therefore, the formation of the mononitroso compound, AH, can be observed in very diluted nitrite solutions with the concentration of 5-MR several orders higher. As previously established [2], cobalt cations form the complex CoA_3 with AH, and the iron(II) cations – FeA_2 . According to the precipitation reaction, the corresponding indissoluble salts should be $\text{Co}(\text{CoA}_3)_2$ and $\text{Fe}(\text{FeA}_2)_2$.

Table 3. Estimation of β and ε_3 ($C_N = 5E-5M$, $C_{AR} = 0.01M$, $C_{Me} = 0.002M$)

| pH | E | $[H^+]$ | $(x_3 + x_4)$ (Eq. (13)) | x_2 (Eq. (11)) | β (Eq. (15)) | $(\beta_{mean} - \beta)^2$ | E_{calc} (Eq. (16)) |
|---|-------|----------|-----------------------------|---------------------|-----------------------|----------------------------|--------------------------|
| CoA ₃ , for $\varepsilon_3 = 22,000$ | | | | | | | |
| 2 | 0.072 | 0.01 | 8.22E-07 | 2.47E-06 | 2.73E+13 | 1.84E+26 | 0.065 |
| 2.2 | 0.087 | 0.00631 | 1.58E-06 | 3.62E-06 | 1.67E+13 | 8.57E+24 | 0.083 |
| 2.4 | 0.112 | 0.003981 | 2.86E-06 | 5.01E-06 | 1.13E+13 | 5.78E+24 | 0.121 |
| 2.6 | 0.171 | 0.002512 | 5.97E-06 | 5.75E-06 | 1.57E+13 | 3.87E+24 | 0.165 |
| 2.8 | 0.203 | 0.001585 | 7.61E-06 | 6.98E-06 | 1.12E+13 | 6.50E+24 | 0.211 |
| 3 | 0.245 | 0.001 | 9.81E-06 | 7.29E-06 | 1.27E+13 | 1.14E+24 | 0.248 |
| 3.2 | 0.272 | 0.000631 | 1.12E-05 | 7.66E-06 | 1.24E+13 | 1.70E+24 | 0.275 |
| 3.4 | 0.298 | 0.000398 | 1.25E-05 | 7.28E-06 | 1.62E+13 | 5.92E+24 | 0.295 |
| 3.6 | 0.322 | 0.000251 | 1.36E-05 | 6.24E-06 | 2.81E+13 | 2.06E+26 | 0.309 |
| 3.8 | 0.37 | 0.000158 | 1.61E-05 | 1.42E-06 | 2.83E+15 | 7.90E+30 | 0.321 |
| 4 | 0.384 | 0.0001 | 1.64E-05 | 6.09E-07 | 3.64E+16 | 1.32E+33 | 0.331 |
| 4.2 | 0.4 | 6.31E-05 | 1.67E-05 | -1.20E-07 | -4.80E+18 | 2.30E+37 | 0.344 |
| Σ : | | | | | 9.62E+13 | 3.35E+25 | |
| Mean: | | | | | 1.37E+13 | 4.78E+24 | |
| s_β , %: | | | | | 15.9 | | |
| FeA ₂ , for $\varepsilon_3 = 9,080$ | | | | | | | |
| 2 | 0.099 | 0.01 | 6.06E-06 | 1.97E-06 | 7.82E+08 | 5.20E+11 | 0.099 |
| 2.2 | 0.126 | 0.00631 | 9.71E-06 | 2.44E-06 | 8.14E+08 | 9.27E+14 | 0.125 |
| 2.4 | 0.153 | 0.003981 | 1.32E-05 | 2.85E-06 | 8.10E+08 | 7.25E+14 | 0.152 |
| 2.6 | 0.175 | 0.002512 | 1.58E-05 | 3.31E-06 | 7.22E+08 | 3.76E+15 | 0.177 |
| 2.8 | 0.199 | 0.001585 | 1.84E-05 | 3.42E-06 | 7.87E+08 | 1.17E+13 | 0.198 |
| 3 | 0.217 | 0.001 | 1.98E-05 | 3.65E-06 | 7.46E+08 | 1.37E+15 | 0.218 |
| 3.2 | 0.235 | 0.000631 | 2.11E-05 | 3.59E-06 | 8.21E+08 | 1.46E+15 | 0.235 |
| 3.3 | 0.244 | 0.000501 | 2.17E-05 | 3.40E-06 | 9.38E+08 | 2.39E+16 | 0.242 |
| 3.4 | 0.298 | 0.000398 | 2.80E-05 | -3.48E-06 | 1.16E+09 | 1.38E+17 | 0.249 |
| 3.5 | 0.334 | 0.000316 | 3.19E-05 | -8.74E-06 | 2.09E+08 | 3.30E+17 | 0.254 |
| Σ : | | | | | 5.48E+09 | 8.26E+15 | |
| Mean: | | | | | 7.83E+08 | 1.18E+15 | |
| s_β , %: | | | | | 4.39 | | |

Estimation of β and ε_3

The experimental data of E and pH from Table 3 and the dissociation characteristics for AH and CoA₃ from Tables 1 and 2 were applied to compute β and ε_3 for CoA₃ by Algorithm (15) in Microsoft Excel. For this aim, various values of ε_3 were fed until the least squares dispersion of β from its mean was obtained at various pH values. At that, for every ε_3 the values of $(x_3 + x_4)$ were calculated using Equation (13). The computation gives the most suitable molar extinction coefficient, $\varepsilon_3 = 22,000$ in the pH region 2–3.4, resulting in the value $1.37(\pm 0.22) \times 10^{13}$ for β . A systematic illogical de-

crease in x_2 and increase in β with increasing pH is revealed above pH 3.4 inasmuch as the solutions turned turbid. The turbid region is shadowed in the tables and is excluded in the calculations of dispersion percentages, s_β .

Estimation of β and ε_3 for FeA_2 was carried out following the same procedure as for CoA_3 . The computation gives for ε_3 of FeA_2 in the region pH 2–3.2 the best value 9,080, which results in the value $7.83(\pm 1.33) \times 10^8$ for β . Analogous to the cobalt complex, homogeneous turbidity was evident before the precipitate fell out in the solutions. Likewise, the inconsistent decrease in x_2 and increase in β were obtained using Equations (13) and (15) for the turbid solutions between pH 3.4–3.5. Contributions of the dissoluble colloidal species will be discussed below.

The theoretical data for E in real solutions computed by Algorithm (16) using the constants and coefficients found are presented in the last column of Table 3. The theoretical results agree satisfactory with the corresponding experimental data in the second column.

When pH exceeded 3.5 for $\text{Fe}(\text{FeA}_2)_2$ and 4.2 for $\text{Co}(\text{CoA}_3)_2$, the photometric method was unsuitable since a flake precipitate formed.

Estimation of P and ε_5

The turbid solutions were modelled by Algorithm (26). Table 4 presents the course of the calculations where the solvation product, P , was computed as the value enabling the least dispersion percentage of ε_5 from its mean under the pH region examined. At first, the unchangeable x_4 was calculated from Equation (18) for the P values suggested. Thereafter, x_3 , $(x_3 + x_4)$, x_2 , x_1 and x_5 were calculated using the Equations (18)–(22) and (24). Knowing the concentrations of the five types of species and molar extinction coefficients of the soluble species, the value for ε_5 was computed from Equation (26). The computation gave the least dispersion of ε_5 for the colloidal cobalt compound, $\varepsilon_5 = 53,300(\pm 1679)$, when P was 2.43×10^{-16} . It was found that the most fitting molar extinction coefficient for the colloidal iron(II) compound, $\varepsilon_5 = 514,000(\pm 44)$ could be obtained when P was 2.34×10^{-13} .

The theoretical data for E in turbid solutions computed by the algorithm (27) using the constants and coefficients found are presented in the last column of Table 4. The theoretical results agree satisfactory with the corresponding experimental data in the second column.

Table 4. Estimation of ε_5 and P for Turbid Solutions ($C_N = 5E-5M$, $C_{AR} = 0.01M$, $C_{Me} = 0.002M$)

| pH | E | x_3 | $(x_3 + x_4)$ | x_2 | x_1 | x_5 | ε_5 | $(\varepsilon_{mean} - \varepsilon_5)^2$ | E_{calc} |
|--|-------|------------|---------------|------------|------------|-------------|-----------------|--|------------|
| CoA₃; $P = 2.43E - 16$, $x_4 = 3.49E - 07$ | | | | | | | | | |
| 3.4 | 0.298 | 1.26E - 5 | 1.30E - 05 | 7.79E - 6 | 5.66E - 06 | -3.89E - 07 | 3.14E + 04 | 4.78E + 08 | 0.289 |
| 3.6 | 0.342 | 7.96E - 6 | 8.31E - 06 | 6.71E - 6 | 3.08E - 06 | 2.55E - 06 | 5.46E + 04 | 1,676,044 | 0.339 |
| 3.8 | 0.37 | 5.02E - 6 | 5.37E - 06 | 5.80E - 06 | 1.68E - 06 | 4.40E - 06 | 5.34E + 04 | 8,464,398 | 0.370 |
| 4 | 0.384 | 3.17E - 6 | 3.52E - 06 | 5.04E - 6 | 9.20E - 07 | 5.58E - 06 | 5.23E + 04 | 960,675.2 | 0.389 |
| 4.2 | 0.4 | 2.00E - 6 | 2.35E - 06 | 4.40E - 6 | 5.07E - 07 | 6.34E - 06 | 5.29E + 04 | 165,228.5 | 0.403 |
| | | | | | | Σ : | 2.13E + 05 | 2,810,413 | |
| | | | | | | Mean: | 5.33E + 04 | | |
| | | | | | | S_p , %: | 3.15 | | |
| FeA₂; $P = 2.34E - 13$, $x_4 = 1.08E - 05$ | | | | | | | | | |
| 3.3 | 0.244 | 1.00E - 05 | 2.09E - 05 | 3.65E - 06 | 3.34E - 06 | 3.25E - 07 | 2.72E + 04 | 5.88E + 08 | 0.252 |
| 3.4 | 0.298 | 7.96E - 06 | 1.88E - 05 | 3.46E - 06 | 2.52E - 06 | 1.61E - 06 | 5.15E + 04 | 965 | 0.298 |
| 3.5 | 0.334 | 6.32E - 06 | 1.72E - 05 | 3.31E - 06 | 1.91E - 06 | 2.62E - 06 | 5.14E + 04 | 965 | 0.334 |
| | | | | | | Σ : | 1.03E + 05 | 1931 | |
| | | | | | | Mean: | 5.14E + 04 | | |
| | | | | | | S_p , %: | 0.085 | | |

Distribution of the Species

Equations (8)–(12) and (18)–(22) were applied for evaluation of the pH effect on the distribution of various species. Figure 2 illustrates the distribution when the initial concentration of nitrite is $5 \times 10^{-5} \text{M}$, of 5-MR 0.01M and of the metal cation 0.002M. The curves in Fig. 2a demonstrate domination of the corresponding to pH molecular species, AH, CoA_3 or $\text{Co}(\text{CoA}_3)_2$, (curves 1, 3 and 5). At that, the concentrations of the anionic forms, A^- and CoA_3^- (curves 2 and 4), are depressed by the reactions of complex formation and precipitation. A similar distribution of the species is evident in Fig. 2b for the iron (II) compounds. Only, thanks to the smaller P value, the share of the anionic species of the iron complex (curve 4) is higher and that of the indissoluble particles (curve 5) is lower.

Figure 3 demonstrates that the partial contribution of AH and A^- to the total optical density is negligible above pH 3. Under the optimum test conditions established in [1] for the cobalt compounds (pH 4) the colloidal particles $\text{Co}(\text{CoA}_3)_2$ give the main contribution to E (Fig. 3a). Under the optimum conditions established for the iron compounds (pH 3.3) the anionic species FeA_2^- contribute most. When pH exceeds 3.3, the sensitivity of the method increases thanks to the addition of the contribution of $\text{Fe}(\text{FeA}_2)_2$. The latter form is inadvisable since the iron colloidal species are not stable and can precipitate in time.

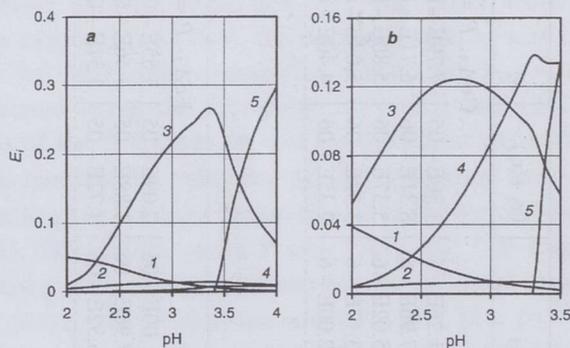


Fig. 3. Effect of pH on the partial contribution of the species from Fig. 2 on E

Conclusions

Alkylresorcinols, the main phenolic compounds obtained at oil shale retorting, can be applied as effective reagents for colorimetric determination of nitrite. An algorithm is deduced to explain the joint effect of the initial concentration of the reagents and pH on the optical density of the nitrite solution tested. The complicated relationship considers contributions of the five coloured species resulted from the acidic dissociations of nitrosoalkylresor-

cinol and the complex, AH , A^- , MeA_n , MeA_n^- , and from the precipitation of an indissoluble salt, $Me(MeA_n)_2$. The theoretical optical densities computed using the acidic dissociation constants, complex stability constants, salt solubility product, and molar extinction coefficients found for 5-methylresorcinol and cobalt or iron(II) sulphate agree with the corresponding experimental results.

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