-OIL SHALE RESORCINOLS – EFFECTIVE REAGENTS FOR NITRITE. AN ALGORITHM FOR THE CONCENTRATION EFFECT

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An algorithm is deduced to describe the effects of nitrite and central cation concentrations on the optical density when nitrite is tested as a nitrosoalkyl-resorcinolate complex. The values of the apparent stability constant and molar extinction coefficient valid at the optimum pH found are estimated for cobalt tri-(4-nitroso-5-methylresorcinolate), cobalt tri-(4-nitroso-2,5-dimethylresorcinolate), iron(II) di-(4-nitroso-5-methylresorcinolate) and iron(II) di-(4-nitroso-2,5-dimethylresorcinolate).

Introduction

Recently a new test method for nitrite as nitrosoalkylresorcinolate was developed [1]. The method is based on the specifically easy nitrosation of alkylresorcinols (R) with nitrous acid formed from nitrite in acidic solutions, and on the subsequent formation of a coloured complex (MeA_n) with a transition metal cation (Me). The main oil shale originated phenols – 5-methyl-resorcinol (5-MR) and 2,5-dimethylresorcinol (2,5-DMR) – were applied as R. The cobalt and iron(II) cations were selected as the most appropriate Me. Experimental plots of optical density (E) versus pH and the initial concentrations of nitrite, R and Me $(C_N, C_R$ and $C_{Me})$ were represented. The curves were obtained under the conditions where only one of the factors was varied and three of them were kept constant (optimal).

In this work, statics of MeA_n formation was described as a result of the joint effect of C_N, C_R, and C_{Me} on E. To solve the problem, a mathematical model of the process was deduced governed by the physical-and-chemical laws being in force at equilibrium conditions. The molar extinction coeffi-

cients and stability constants were estimated for the cobalt and iron complexes of nitrosed 5-MR and 2,5-DMR.

## Theoretical Approach

Reactions

Formation of the coloured complex MeA_n from nitrite is a result of four consecutive reactions. The anionic species of nitrite cannot attack the negatively charged positions of the aromatic ring characteristic to R. So, the protonation reaction

$$NO_2^- + H^+ \Leftrightarrow HNO_2 \qquad\qquad I$$

has to take place for nitrosation

$$HNO_2 + R \Rightarrow AH + H_2O \qquad\qquad II$$
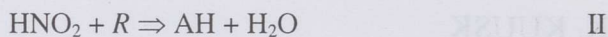
The nitrosoalkylresorcinol formed ($RNO \equiv AH$) is a weak acid whose acidic dissociation

$$AH \Leftrightarrow A^- + H^+ \qquad\qquad III$$
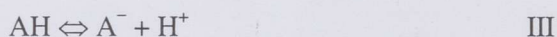
gives the nitrosoresorcinolate anion (A^-) capable for the complex formation

$$nA^- + Me^{+n} \Leftrightarrow MeA_n \qquad\qquad IV$$

Equations

The statics of the complex formation ascertained as the steady state for E in time can be described by the system of the following equilibrium equations:

• Acidic dissociation constants of nitrous acid and nitrosoalkylresorcinol

$$K_1 = [NO_2^-][H^+]/[HNO_2] \qquad\qquad (1)$$

$$K_2 = [A^-][H^+]/[AH] \qquad\qquad (2)$$

• Stability constant of the complex

$$\beta = [MeA_n]/([Me][A^-]^n) \qquad\qquad (3)$$

• Mass balances of the reagents

$$C_R = [R] + [AH] + [A^-] + n[MeA_n] \qquad\qquad (4)$$

$$C_N = [NO_2^-] + [HNO_2] + [AH] + [A^-] + n[MeA_n] \qquad\qquad (5)$$

$$C_{Me} = [Me] + [MeA_n] \qquad\qquad (6)$$

The optical density measured results from the partial absorbencies of the coloured molecular and anionic species of free nitrosoalkylresorcinol and of the complex formed as follows:

$$E = \varepsilon_{AH}[AH] + \varepsilon_A[A^-] + \varepsilon[MeA_n] \qquad (7)$$

where ε is molar extinction coefficient of the corresponding species.

The seven-equation system above contains eleven unknown characteristics:

- five unpublished constants for the nitroso-compounds: K_2, β, ε, ε_{AH}, ε_A
- six equilibrium concentrations: $[NO_2^-]$, $[HNO_2]$, $[A^-]$, $[AH]$, $[MeA_n]$, and $[Me]$.

The known characteristics are: the initial concentrations of the reagents, the values of optical density and pH estimated under any condition tested, and the acidic dissociation constant for nitrous acid, $pK_1 = 3.37$ [2].

Effect of C_R

An excess of alkylresorcinol is obligatory for the test method of nitrite studied. When C_R is lower than C_N, the nitrosation process is too slow for testing diluted nitrite solutions. Besides, due to the by-reactions, such as decomposition of nitrous acid and formation of dinitrosoalkylresorcinols, the quantity of MeA_n formed is not proportional to the nitrite concentration.

According to the Reaction II, nitrosation is an irreversible process. Consequently, the alkylresorcinol concentration should effect mainly the nitrosation rate. When the steady state of E in time is attained with a sufficient excess of alkylresorcinol, nitrite should be totally converted into the respective nitrosoalkylresorcinol. So, the equality

$$C_{AH} \equiv C_N \qquad (8)$$

should be in force.

Effect of C_{Me}

With a goal to eliminate some unknown characteristics for the complex formation, the apparent constants ε_H and β_H valid at the proton concentration $[H^+]$ only were applied. Besides, considering that under the test-conditions suggested in [1], consumption of complexing cations for complex formation is some orders lower than C_{Me}, the approximation

$$[Me] = C_{Me} \qquad (9)$$

was used.

Consequently, Equations (1)–(3) as well the constants K_2, ε_{AH} and ε_A may be ignored. Co-solution of Equations (4)–(9) remained gives the expression

$$\beta_H = E\varepsilon_H{}^{n-1}/C_{Me}/(C_N\varepsilon_H - nE)^n \qquad (10)$$

where C_{Me}, C_N and E are the known variables.

The two unknown constants, ε_H and β_H, can be easily found through rearrangement of Equation (10) as

$$(E/C_{Me})^{1/n} = (\beta_H \, \varepsilon_H)^{1/n} \, C_N - n\beta_H^{1/n} \, \varepsilon_H^{-2/n} \, E \qquad (11)$$

When C_N is kept constant, Equation (11) must represent a linear regression

$$Y = A - BX \qquad (12)$$

where the variable is the optical density measured at various C_{Me}

$$X = E \qquad (13)$$

and the function value is calculated from the optical density and the cation concentration being varied by

$$Y = (E/C_{Me})^{1/n} \qquad (14)$$

The intercept A and the slope B of the plot of Y versus E are formed from the unknown constants as follows

$$A = (\beta_H \, \varepsilon_H)^{1/n} \, C_N \qquad (15)$$

$$B = n\beta_H^{1/n} \, \varepsilon_H^{-2/n} \qquad (16)$$

Consequently, the constants ε_H and β_H can be calculated using A and B from the equations

$$\varepsilon_H = (nA/B/C_N)^{n/3} \qquad (17)$$

$$\beta_H = A^n/\varepsilon_H/C_N^n = (A^2 B/n/C_N^2)^{n/3} \qquad (18)$$

Effect of C_N

Equation (11) describes the complicated relationship between E, C_N and C_{Me}. Nevertheless, the established values of ε_H and β_H allow computing E at any concentration of nitrite and Me. Furthermore, for any C_{Me} the lower limit of C_N can be calculated as

$$C_N(min) = -a/b \qquad (19)$$

where a and b are the coefficients of the linear treadline for the plot of E versus C_N

$$E = a + bC_N \qquad (20)$$

Experimental Results and Discussion

Effect of C_{Me}

The Table represents the experimental data for calculation of ε_H and β_H taken from our previous paper [1]. The values of optical density were measured at equilibrium conditions (after the reaction time 24 h) versus concentration of cobalt sulfate and iron(II) sulfate when 5-MR and 2,5-DMR were applied. In all the series the initial concentration of nitrite

was 5×10^{-5}M, and of alkylresorcinols 0.01M. The pH value was adjusted with acetate-acetic acid buffer solutions close to the optimum, $pH_{Co} = 4.0$ and $pH_{Fe} = 3.3$.

**Concentration Effect of Cations on the Optical Density**
($C_N = 5 \times 10^{-5}$M, $C_R = 0.01$M, $pH_{Co} = 4.0$; $pH_{Fe} = 3.3$)

| Characteristics and constants	Cobalt				Iron			
	5-MR		2,5-DMR		5-MR		2,5-DMR	
	E	Y	E	Y	E	Y	E	Y
C_{Mc}, M, × 10³:								
0.25	1.277	17.22	0.616	13.47	0.579	48.12	0.579	48.12
0.5	1.494	14.40	0.745	11.39	1.083	46.5	1.084	46.6
0.75	1.609	12.90	0.816	10.26	1.142	39	1.142	39
1	1.686	11.90	0.914	9.7	1.203	34.7	1.231	35.1
1.5	–	–	–	–	1.318	29.6	1.282	29.2
2	1.907	9.84	0.986	7.9	1.373	26.2	1.35	26
3	1.907	8.58	0.985	6.89	1.382	21.5	1.42	21.8
4	1.975	7.89	1.024	6.33	1.399	18.7	1.403	–
5	1.99	7.34	1.023	5.9	–	–	–	–
6	2.093	7.04	1.108	5.69	1.4048	15.3	1.386	–
8	2.115	6.41	1.139	5.22	1.28	–	1.291	–
10	2.115	5.93	1.175	4.90	1.254	–	1.263	–
n	3		3		2		2	
A, M$^{-1/n}$	33.95		23.50		126.9		122.3	
B, M$^{-1/n}$	13.09		16.21		75.49		71.39	
r	0.994		0.980		0.976		0.989	
β_H, M^{-n}	2.012×10^{12}		1.193×10^{12}		3.89×10^9		3.57×10^9	
ε_H	1.556×10^5		8.70×10^4		1654		1675	

Figure 1 proves that when the value of n is 2 for iron complexes, and 3 for cobalt complexes, the plots of the auxiliary function Y (Equation (14)) versus E submit the linear dependence described by Equations (11) and (12).

Fig. 1. Plot of the auxiliary function Y versus optical density: ● and ○ are cobalt complexes, ▲ and △ are iron complexes; ● and ▲ – 5-MR, ○ and △ – 2,5-DMR. Calculated curves: "—" – 5-MR, "- -" – 2,5-DMR
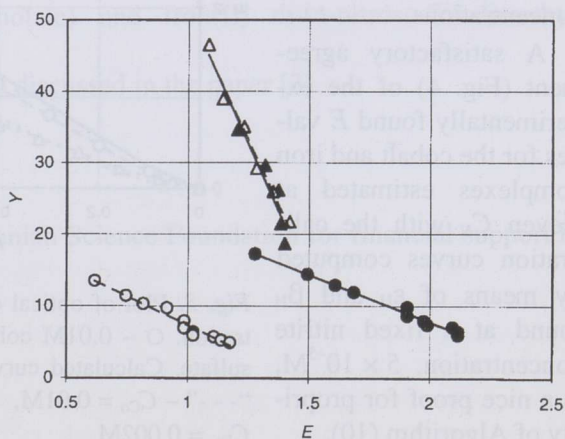
The four last rows of the Table give coefficients of the linear regression, A and B, and the values of ε_H and β_H calculated by Equations (17) and (18) for the four complexes studied. The results evidence that the apparent stability constants and molar extinction coefficients of the cobalt complexes significantly surpass those of the iron complexes. At that, the characteristics of cobalt complexes for 5-MR are 1.7–1.8 times higher than those for 2,5-DMR. The characteristics of iron complexes have close values for 5-MR and 2,5-DMR.

Figure 2 shows a satisfactory agreement (correlation coefficient, $r = 0.998$–0.999) of the E values estimated at various C_{Me} (see the Table) with the curves computed by Equation (10) using the values of ε_H and β_H established.
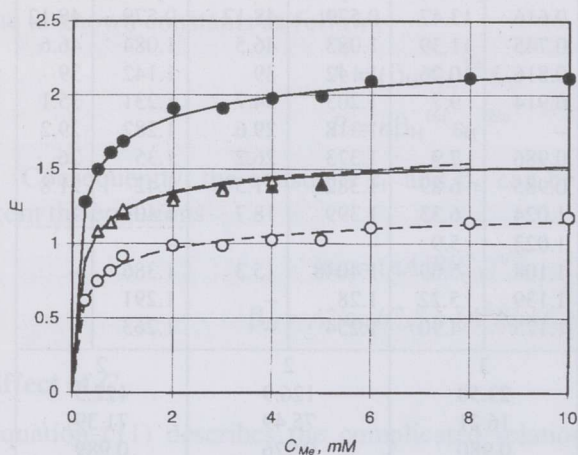
The agreement of the experimental and predicted results in Fig. 2 should be expected as the constants found were applied for the system used in computation.

Fig. 2. Plot of optical density versus cation concentration. The marks see in Fig. 1

Effect of C_N

Figure 3 depicts the experimental and calculated E values at various nitrite concentrations.

A satisfactory agreement (Fig. 4) of the experimentally found E values for the cobalt and iron complexes estimated at eleven C_N with the calibration curves computed by means of ε_H and β_H found at a fixed nitrite concentration, 5×10^{-5}M, is a nice proof for propriety of Algorithm (10).
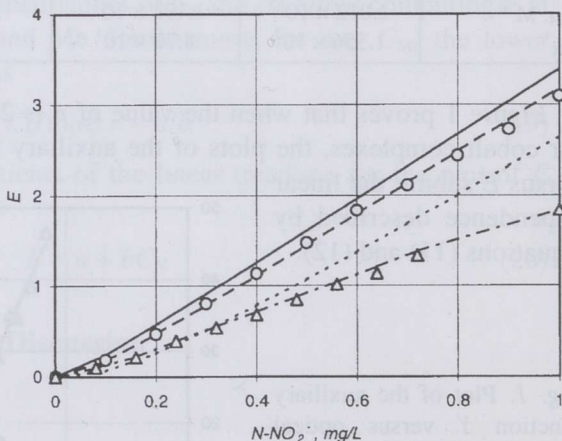

Fig. 3. Plot of optical density versus nitrite concentration. $\bigcirc$ – 0.01M cobalt sulfate, $\triangle$ – 0.002M iron sulfate. Calculated curves "·····" – $C_{Co} = 0.001$M, "- - -" – $C_{Co} = 0.01$M, "—" – $C_{Co} = 0.05$M, "-··-" – $C_{Fe} = 0.002$M

Both experimental and computed plots reveal a concave part in the beginning of the calibration curves due to the insufficient complex formation. Because of the different n values, the iron complexes obtain lower concentration limit for nitrite (Equation (19)) than the cobalt complexes, in spite of their lower values of ε_H and β_H. For example, $C_N(min)$ for 0.002M C_{Fe} is 0.024 mg/L, but for five times higher concentration of cobalt, reaches 0.044 mg/L.

Fig. 4. Comparison of the experimental and calculated optical densities for cobalt (O) and iron (Δ) complexes

The concavity and therefore $C(min)$ decrease when C_{Me} increases. For example, the calculated curves of 0.001, 0.01 and 0.05M cobalt sulfate (depicted as dotted curves in Fig. 3) predict for $C(min)$ the values 0.083, 0.044 and 0.0075 mg/l, respectively. A limitation to use the higher C_{Me} lies in an increase in the background optical density.
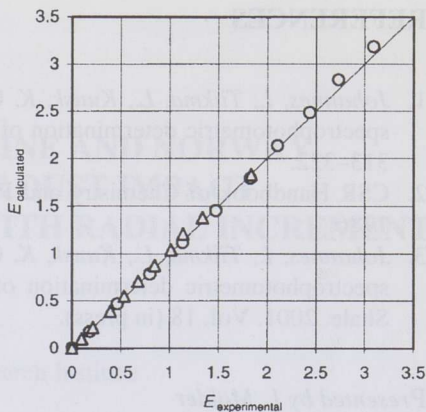
Conclusions

A theoretical basis for the new test method of nitrite was created, based on the nitrosation reaction of alkylresorcinols with nitrous acid and on the following formation of a coloured complex with a transition metal cation. An algorithm was deduced to describe the effects of nitrite and central cation concentrations on the optical density at static conditions. The values of the apparent stability constant and molar extinction coefficient, being valid at the optimum pH found, were estimated for cobalt tri-(4-nitroso-5-methyl-resorcinolate), cobalt tri-(4-nitroso-2,5-dimethylresorcinolate), iron(II) di-(4-nitroso-5-methylresorcinolate) and iron(II) di-(4-nitroso-2,5-dimethyl-resorcinolate).

The effect of pH will be discussed in the paper [3].

Acknowledgements

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