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Analytica Chimica Acta 362 (1998) 121–129

ANALYTICA CHIMICA ACTA

Synthesis and spectroscopic properties of new luminol-linked calixarene derivatives

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Received 15 August 1997; received in revised form 22 December 1997; accepted 12 January 1998

Abstract

Syntheses of luminol-linked calixarene derivatives, *p*-(2,3-dihydro-1,4-phthalazinedione-5-azo)calix[n]arenes (n=4, 6, 8: (3a), (3b) and (3c), respectively), are described together with their spectroscopic properties for analytical purposes. It is found that the synthesized derivatives have a good solubility in basic aqueous media and possess multi-optical functions. In alkaline media of pH 11.5 containing 10 μg ml^{-1} of Cu(II), the calixarenes react with H_2O_2 to emit light of wavelength 420 nm. Various parameters such as acidity, order and amounts of reagent addition for H_2O_2 chemiluminescent determination are optimized. Among these calixarenes, (3a) is the most sensitive one with a detection limit of 0.01 μg ml^{-1} H_2O_2, and its chemiluminescence intensity is directly proportional to the concentration of H_2O_2 in the range 0.01–5 μg ml^{-1}. Additionally, the calixarenes fluorescence properties similar to that of luminol do not seem important because of not causing any great spectral change upon addition of H_2O_2, Ag^+, Co^{2+}, Cr^{3+}, Cu^{2+} or Fe^{2+}, but the absorption spectrum of (3a) gives a specific response to Ag^+, making it of potential use as a chromogenic reagent for Ag^+ detection. © 1998 Elsevier Science B.V.

Keywords: Chemiluminescence; Spectrophotometry; Hydrogen peroxide; Silver; Calixarene

1. Introduction

Calixarenes, which appeared after crown ethers and cyclodextrins as the third generation of inclusion compounds, are macrocyclic phenol–formaldehyde condensation products [1,2]. They are noted for their ability to form host–guest complexes by trapping organic compounds, small ions, and gases in their toruslike cavities as well as to mimic enzyme functions. Because of the great advantage of calixarenes in respect of facile synthesis and versatile molecular structures in comparison to crown ethers and cyclodextrins, a variety of new functionalized host molecules have been prepared and employed successfully in many fields, including recovery of metal ions, separation of neutral organic molecules and pollution control [3]. More recently, a great deal of interest has been shown in synthetic chromogenic and fluorogenic calixarenes for determining various guests such as Li^+, Na^+, K^+, Ca^{2+}, UO_2^{2+} and organic amines [4–6]. However, most of these studies had to be conducted in organic media due to the poor solubility of the functionalized calixarenes in aqueous media. From the analytical point of view this is a disadvantage, and therefore water-soluble spectroscopic calixarenes are desirable. Furthermore, very few chemiluminescent

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PII S0003-2670(98)00050-6

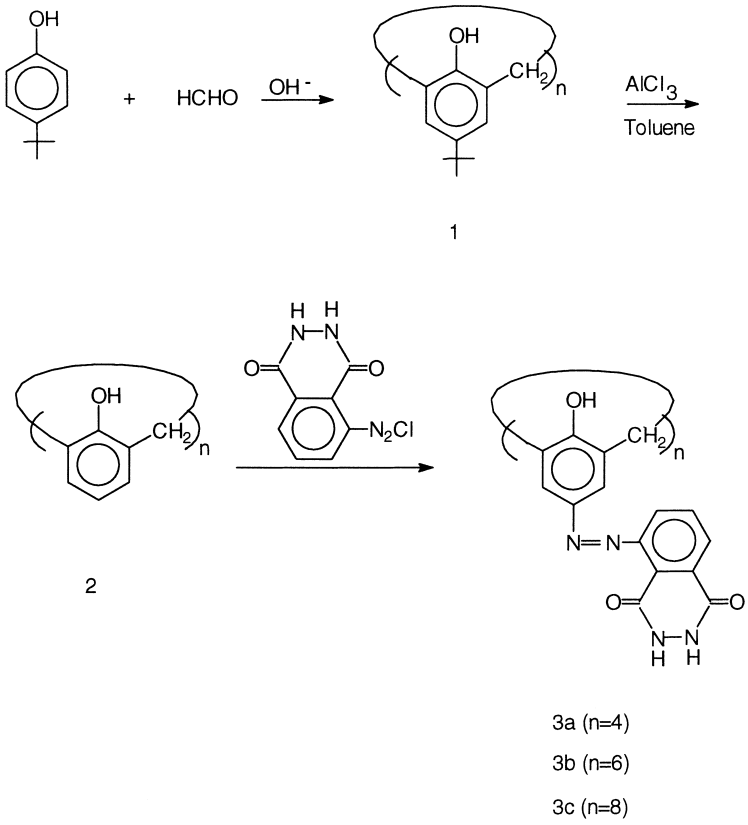

Fig. 1. Synthesis of *p*-(2,3-dihydro-1,4-phthalazinedione-5-azo)calix[n]arenes (3).

calixarenes [7,8] have so far been prepared although a chemiluminescent method is generally more sensitive than an absorption one. Obviously, it is necessary to develop new calixarenes which possess not only good solubilities in aqueous media but also specific spectroscopic properties such as chemiluminescent properties. Luminol is a well-known luminescent and fluorescent reagent and may be important in this area, because it has an amino group which can be diazotized and then coupled with phenol [9], and its optical properties can be perturbed significantly by chemical stimuli such as an environmentally important oxidant H_2O_2. Also, luminol is easily soluble in basic aqueous media, this property may play a role in improving calixarene solubility in aqueous media. Thus, in this work, luminol-linked calixarene derivatives, *p*-(2,3-dihydro-1,4-phthalazinedione-5-azo)calix[n]arenes (n=4, 6, 8: 3a, 3b and 3c, respectively), have been synthesized (Fig. 1), and spectroscopic properties evaluated for their potential use.

2. Experimental

2.1. Apparatus

Infrared spectra were taken in KBr disks on a BIO-RAD FTS-7 spectrometer. ^{1}H NMR spectra were recorded on a Bruker AM-360 spectrometer at 360 MHz using tetramethylsilane as an internal standard. Thin-layer chromatographic (TLC) analysis was performed on Merck 60 F_{254} silica gel plates (absorbent thickness 0.25 mm), using a 1 : 1 : 1 mixture of *N*,*N*-dimethylformamide (DMF)/ethyl acetate/toluene as eluent. Uncorrected melting points were measured on a Jürgens electrothermal apparatus.

UV/VIS spectra were taken on a Varian DMS 100S spectrophotometer. Fluorescence spectra were recorded as raw data with an AMINCO SPF-500 spectrofluorimeter in 10×10 mm quartz cells; a spectral bandwidth of 10 nm was used in both, excitation and emission monochromator. Chemiluminescence spectra were recorded on the same instrument, employing fast scanning rates and wide slits (40 nm band path) with the excitation source off. An Ionalyzer 701A pH meter (Orion) was used for pH measurements. All measurements were carried out at 23±2°C.

2.2. Chemicals and solutions

A 0.1% (m/v) of (3a) solution (8.5×10^{-4} mol l^{-1}) was prepared in dilute sodium hydroxide (pH 11.0). The dilute hydrogen peroxide standards were freshly prepared by diluting an aqueous 30% H_2O_2 stock solution (Merck) that was standardized against standard potassium permanganate (sodium oxalate was the primary standard) [10]. 1.0 mg ml^{-1} of copper(II) and silver(I) stock solutions, and 0.1 mol l^{-1} of Na_2HPO_4–NaOH buffer solutions (pH 11.0 and 11.5) were also employed. Toluene was dried over P_2O_5 and distilled before use. All other reagents were obtained from Merck, Fluka or Riedel-de Haen, and used without further purification.

2.3. Synthesis of p-(2,3-dihydro-1,4-phthalazinedione-5-azo)calix[n]arene

2.3.1. p-tert-butylcalix[n]arene (1)

The synthesis of compound (1) was performed according to the method available in literature [11].

2.3.2. Calix[n]arene (2)

Following a similar method to that of Gutsche et al. [12], compound (2) was prepared by $AlCl_3$-catalyzed de-*tert*-butylation of compound (1) at 40°C for 3 h.

2.3.3. p-(2,3-dihydro-1,4-phthalazinedione-5-azo)calix[n]arene (3)

(*3a*): To a solution of luminol (1.45 g, 8 mmol) dissolved in 20 ml of 0.5 mol l^{-1} NaOH, 10 ml of 4 mol l^{-1} HCl was added with constant stirring. The freshly precipitated luminol was cooled to 0–5°C and diazotized with 5 ml of $NaNO_2$ (0.56 g, 8 mmol) solution. After half-an-hour stirring, a clear brown solution of diazo salt was obtained. A little urea (~0.2 g) was then added and the solution was stirred for a further 10 min. Then, the diazo-salt solution was slowly added to a stirred mixture of $CH_3CO_2Na\cdot3H_2O$ (1 g) and calix[4]arene (0.85 g, 2 mmol) in 50 ml DMF under ice cooling. The red reaction mixture was allowed to couple for 2 h at pH 6–8 in an ice bath and then poured into water (250 ml). The resulting solution was acidified to pH ~1 with HCl, and a large quantity of the dark red precipitate formed was then filtered and washed with water. After drying, the crude product weighed 1.8 g, which was purified twice by dissolving in pyridine (90 ml) and reprecipitating with 4 mol l^{-1} HCl (~270 ml), followed by washing with water. The purified product (1.2 g, 51% yield) was obtained as a reddish brown solid (mp>300°C), which is easily soluble in pyridine, DMF and alkaline solution, but not in water, ethanol, and $CHCl_3$. TLC analysis gave a single spot with R_f=0.83. IR (cm^{-1}): 3300–3000 (brs, OH, NH); 1649 (lactam C=O); 1594, 1509 (C=C, N=N). ^{1}H NMR(pyridine-d_5): 10.15 (brs, 4H, OH), 8.53–6.55 (m, 20H, Ar–H), 4.1 (d, 8H, $ArCH_2Ar$).

(*3b*): This compound was prepared and purified as described above for (3a), starting from luminol (1.1 g, 6 mmol), $NaNO_2$ (0.42 g, 6 mmol) and calix[6]arene (0.64 g, 1 mmol). The yield of the dark red product (3b) was 1.2 g (68%), mp>300°C. The solubility behavior is similar to that of (3a). TLC analysis gave a single spot with R_f=0.80. IR(cm^{-1}): 3300–3000 (brs, OH, NH); 1648 (lactam C=O); 1593, 1508 (C=C, N=N). ^{1}H NMR (pyridine-d_5): 9.15 (brs, 6H, OH), 8.3–6.6 (m, 30H, Ar–H), 4.3–3.8 (m, 12H, $ArCH_2Ar$).

(*3c*): This calixarene was synthesized and purified as described above for (3a), starting from luminol (1.1 g, 6 mmol), $NaNO_2$ (0.42 g, 6 mmol) and calix[8]arene (0.64 g, 0.75 mmol). The yield of the reddish brown product (3c) was 1.1 g (62%), mp>300°C. Its solubility behavior is also similar to that of (3a). TLC analysis showed a spot with R_f=0.82. IR (cm^{-1}): 3300–3000 (brs, OH, NH); 1648 (lactam C=O); 1593, 1508 (C=C, N=N). ^{1}H NMR (pyridine-d_5): 8.3–6.8 (m, 40H, Ar–H), 5.5 (brs, 16H, NH), 4.1 (brs, 16H, $ArCH_2Ar$).

2.4. Procedure for examining spectroscopic properties

2.4.1. Chemiluminescence

The chemiluminescence reaction in a quartz cell was started by injecting 0.1 ml of 200 μg ml^{-1} Cu(II) solution into 1.9 ml of H_2O_2 sample solution containing 0.6 ml of Na_2HPO_4–NaOH buffer (pH 11.5) and 60 μl of 8.5×10^{-4} mol l^{-1} (3a) (or (3b), or (3c)). At the same time, the chemiluminescent spectra were recorded or peak chemiluminescent intensities measured at 420 nm.

2.4.2. Fluorescence

A solution containing 0.03 mol l^{-1} Na_2HPO_4–NaOH buffer (pH 11.5) and 2.1×10^{-6} mol l^{-1} of (3a) (or (3b) or (3c)) was used for fluorescence tests. The fluorescence spectra or intensities were determined at λ_{ex}=310 nm or/and λ_{em}=410 nm, with a bandpass of 10 nm at the entrance and exit slits.

2.4.3. UV-visible absorption

To a test solution containing not more than 70 μg of silver(I), 3.0 ml of pH 11.0 aqueous buffer solution (Na_2HPO_4–NaOH) and 1.5 ml of 0.1% (3a) were added, and the final volume adjusted to 10 ml with water. The absorbances were measured at 460 nm in 1 cm cells against the reagent blank.

3. Results and discussion

3.1. Synthesis and identification of compound (3)

Calixarenes, in general, have a low solubility in aqueous media, which is important for serving as phase-transfer agents or extractants. For spectroscopic analysis, however, such a property is undesirable because organic solvents or surfactants have to be used in these cases. In this study, we try to link luminol to calixarene, since luminol has not only an emission site of phthalhydrazide but also a good solubility in alkaline aqueous media. It is expected that the prepared calixarenes would have some useful analytical properties such as multi-optical functions and improved solubility.

There have been several papers which revealed that a diazo-coupling reaction proceeds readily between calix[n]arene and various diazonium salts, affording a completely *p*-position-substituted derivative as a main product due to the strong hydrogen-bonding effect among the calixarene OH groups [13–17]. It is found that the diazotized luminol is also easily coupled with calix[n]arene to yield a reddish brown product, which can be identified on the basis of IR and NMR spectral data. The stretching frequencies of the OH groups appear at low frequency, which can be explained by the strong intramolecular hydrogen bonding present in the derivative. The carbonyl group of lactam shows an intense characteristic absorption band at 1649–1648 cm^{-1}. It should be noted that, sometimes, the NH protons of lactam cannot be observed in pyridine by NMR, presumably due to exchange.

The prepared compounds have a good solubility in alkaline aqueous media. For instance, the solubilities of (3a), (3b) and (3c) in 0.02 mol l^{-1} NaOH are 0.36, 0.28 and 0.24% (m/v) at 25.0°C, respectively, which are much larger than those (<0.02%) of the calix[n]arenes (n=4, 6, 8) themselves. This enables the new derivatives to be used directly in aqueous media rather than in organic media.

3.2. Chemiluminescent properties

3.2.1. Chemiluminescent spectra and effect of pH

Like luminol, compound (3) reacts with an oxidant in the presence of a catalyst in alkaline medium to emit light with a wavelength of 420 nm, which is 10 nm shorter than 430 nm of luminol (Fig. 2, each curve in Fig. 2 represents the average of 2–3 runs). Although a variety of oxidants such as permanganate and iodine can be used, the environmentally important and most common agent H_2O_2 was employed here. The catalytic effect of metal ions varied in the following order: Cu^{2+} (chemiluminescence intensity in the presence of Cu^{2+} was taken as 100%) > Fe^{2+} (52%) > Co^{2+} (3%) > Cr^{3+} (1%). So, Cu^{2+} was selected as a catalyst for the present system. Time-course profiles of the chemiluminescence production (Fig. 3) show that (3a) is the most sensitive one to H_2O_2 among these calixarenes, although all of them are inferior to luminol. Therefore, (3a) was employed to further study the chemiluminescent assay for H_2O_2. Fig. 3 also indicates that the chemiluminescent reaction is rapid and suitable to perform a peak analysis.

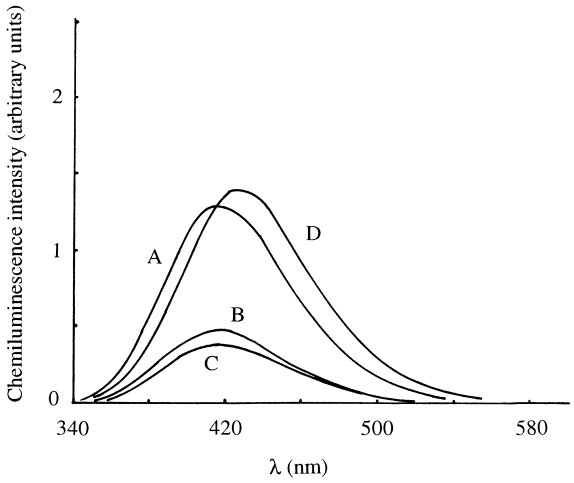

Fig. 2. Chemiluminescence spectra of 2.55×10^{-5} mol l^{-1} of (A) 3a, (B) 3b, (C) 3c, and 2.55×10^{-6} mol l^{-1} of (D) luminol in the presence of 10 μg ml^{-1} Cu^{2+} in alkaline media (pH 11.5). Range scale 10; scan rate 500 nm/min; $[H_2O_2]$=1 μg ml^{-1} for all experiments.

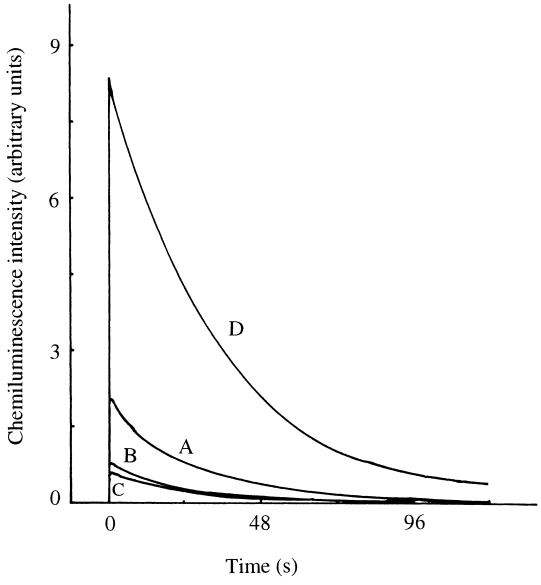

Fig. 3. Chemiluminescence intensity–time profiles of 2.55×10^{-5} mol l^{-1} of (A) 3a, (B) 3b, (C) 3c and (D) luminol. Range scale 100; other conditions same as in Fig. 2.

The maximum intensity of light emission was achieved in the pH range 11.0–11.7 (Fig. 4). Therefore, pH 11.5±0.2 may be used and maintained with aqueous Na_2HPO_4–NaOH buffer, whose optimum

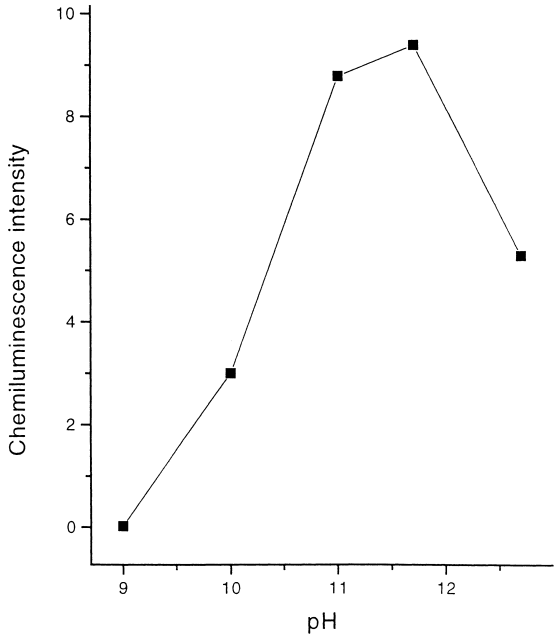

Fig. 4. Effect of pH on chemiluminescence intensity of 2.55×10^{-5} mol l^{-1} of (3a). $[H_2O_2]$=3 μg ml^{-1}.

amount was 0.6 ml for 2 ml of test solution. Other buffers, such as NaOH–KCl gave an identical result as with Na_2HPO_4–NaOH although $Na_2B_4O_7$–NaOH caused a significant decrease (11%) in chemiluminescence intensity.

3.2.2. *Effects of reagent concentration and addition order*

For the determination of 1.0 μg ml^{-1} H_2O_2, the chemiluminescence intensity reached a maximum with the final concentration ranges of 1.3–4.3×10^{-5} mol l^{-1} for (3a) and 5–15 μg ml^{-1} for Cu^{2+}. In this work, 2.55×10^{-5} mol l^{-1} of (3a) and 10 μg ml^{-1} of Cu^{2+} were used, respectively. Reagent addition order, including (3a), H_2O_2 and Cu^{2+} was examined. The typical procedure involved the addition of two required reagent combinations (e.g. 3a–H_2O_2, Cu^{2+}–H_2O_2 and 3a–Cu^{2+}) into the cell and mixing well before injection of the third reagent. It was found that (3a) and H_2O_2 were indispensable and the peak height intensity was the largest on injecting Cu^{2+} last.

3.2.3. *Effects of temperature and time*

The light intensity did not depend on the standing time (up to 3 h) of the mixed test solution before

injecting Cu^{2+} solution. However, temperature has an appreciable effect on the light emission. For example, relative light intensities for 1 μg ml^{-1} H_2O_2 were 1.52, 2.87 and 2.20 at 10, 23 and 32°C, respectively. In this study, the temperature was maintained at 23±2°C.

3.2.4. Linearity

The linear range of the system for H_2O_2 was 0.01–5 μg ml^{-1}, and the regression equation (peak height signals) was determined to be:

$$I(\text{chemiluminescence intensity}) = 3.249 \cdot C(\mu\text{g } H_2O_2\,\text{ml}^{-1}) - 0.401,$$
$$n = 6,\ r = 0.998.$$

The precision was checked by repeated determinations (n=10) using 1 μg ml^{-1} H_2O_2 test solution. The relative standard deviation was 4.7%. The detection limit for H_2O_2 was 0.01 μg ml^{-1} (S/N=3).

3.2.5. Influence of foreign substances

The potential interferences of more than 20 substances were tested for the present system. The tolerable amount was that of a species which gives a relative error of <±5% in the peak height intensity, i.e., for 10 μg of H_2O_2 in 10 ml of solution, the tolerable amounts of the foreign substances are 15 μg of Ag(I) and Hg(II); 200 μg of Al(III), NO_3^- and V(V); 500 μg of Ca(II), CO_3^{2-} and Mo(VI); 800 μg of Cl^-; 1400 μg of K(I); 50 μg of Mg(II) and Sn(II); at least 1.5 mg of SiO_3^{2-} and SO_4^{2-}; <5 μg of Cr(III), Co(II), Fe(II), Mn(II), Ni(II) and Zn(II). The selectivity of (3a) is similar to that of luminol because both have the same emission site of phthalhydrazide, which can react with an oxidant and can be catalyzed by a number of transition metal ions.

3.2.6. Analytical applications

Hydrogen peroxide is often the focus of environmental and biological studies, and there have been several chemiluminescent methods proposed for its determination [18–23]. 1,2,4-Trichlorobenzene, mainly used as a carrier in textile industry and found as a pollutant in some waters, can be decomposed by UV (254 nm) irradiation in the presence of H_2O_2. In this process H_2O_2 plays an important, cooperative role. As an example of the application, (3a) was attempted for monitoring the concentration changes of H_2O_2 during such a treatment. The results are shown in Table 1.

As can be seen, water was not affected by UV irradiation, whereas the solution containing 1,2,4-Trichlorobenzene (sample 2) did change its property after irradiation, probably producing a small amount of an oxidant (e.g. organic peroxide) which reacts with the phthalhydrazide site to emit light. It is difficult to determine which oxidant is formed due to low concentration, but it can be expressed as the corresponding concentration of H_2O_2 which gives an equivalent oxidation ability. It was found that 70% of H_2O_2 in sample 3 was decomposed after 1 h UV irradiation. The proposed method was also checked for directly determining H_2O_2 in synthetic samples made from tap water and river water, but satisfactory results were not obtained with recoveries up to 69.5% and 24.4% for tap water and river water, respectively.

Table 1
Determination of H_2O_2 in various reaction samples [a]

Sample	Concentration of H_2O_2 (μg ml^{-1})		Recovery (%)
	before irradiation	after 1 h irradiation	
1. H_2O	<0.01	<0.01	—
2. 1+1,2,4-Trichlorobenzene (10 μg ml^{-1})	<0.01	0.09±0.01 [b]	—
3. 2+H_2O_2	186±7 189±2 [d]	55±3	95±2 [c]

[a] Analytical results were expressed as: mean of three determinations±standard deviation.
[b] The value implies production of a substance which had an oxidation ability equivalent to that for this concentration of H_2O_2, rather than the formation of real H_2O_2.
[c] Recovery test was made with the solution after irradiation.
[d] This value was obtained by potassium permanganate titration [10].

Table 2
Fluorescence excitation (ex) and emission (em) maxima and relative intensities of the calixarene derivatives together with luminol at the same concentration of 2.1×10^{-6} mol l^{-1} in a medium of pH 11.5

Reagent	λ_{ex} (nm)	λ_{em} (nm)	Peak fluorescence intensity (arbitrary unit)
(3a)	310	410	30
(3b)	310	410	100
(3c)	310	410	130
Luminol	310 (1st max)	410	110
	365 (2nd max)	410	180

3.3. Fluorescence properties

Under optimum conditions, fluorescence properties of these calixarenes were examined. The results are presented in Table 2. It is seen from the Table 2 that the maximum peak intensities for the calixarene derivatives were obtained at λ_{ex}=310 nm, while for luminol at λ_{ex}=365 nm. The calixarenes are less fluorescent than luminol, possibly owing to the introduction of an electron-withdrawing substituent (azophenyl) [24]. The addition of two reagent combinations (e.g. Cu^{2+}–H_2O_2) into the (3a) solution caused the decomposition of (3a) to emit light, but all the fluorescence properties were hardly affected by the separate addition of H_2O_2 and metal ions such as Ag^+, Co^{2+}, Cu^{2+} and Fe^{2+}, suggesting that the present system is not suitable for fluorimetric determination of these substances.

3.4. UV-visible absorption properties

3.4.1. Absorption spectra

Absorption spectra of (3a) and its silver complex in basic media are shown in Fig. 5. The absorption peak of (3a) is located at 371 nm (curve A) and the complex at 460 nm (curve B).

The molar absorptivities of silver complexes of (3b) and (3c) are 7.9×10^3 l mol^{-1} cm^{-1} (λ_{max}=490 nm) and 8.8×10^3 l mol^{-1} cm^{-1} (λ_{max}=515 nm), respectively, both of which are lower than 1.3×10^4 l mol^{-1} cm^{-1} (λ_{max}=460 nm) of (3a).

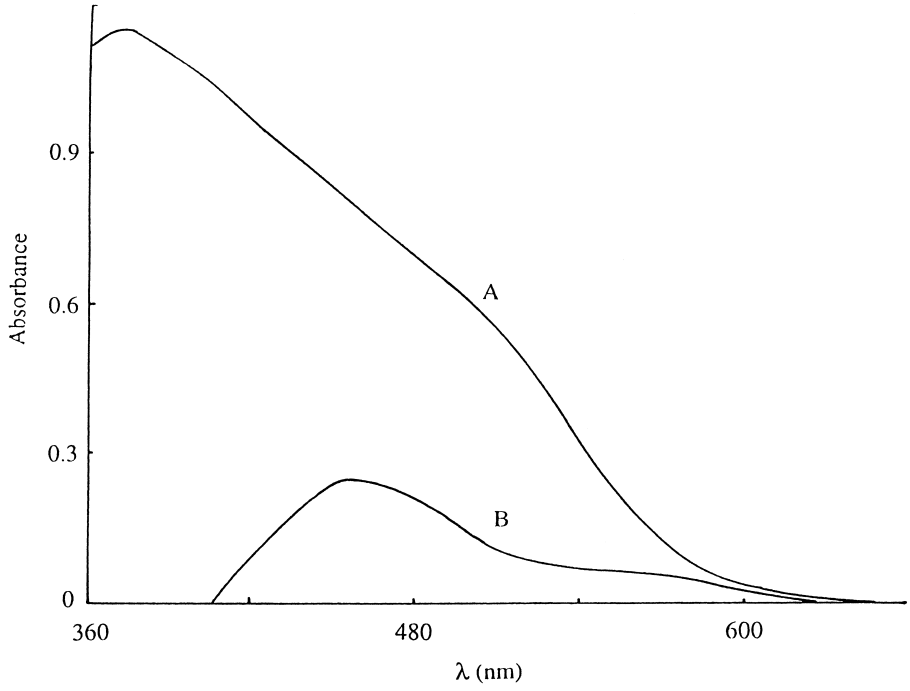

Fig. 5. Absorption spectra of (3a) and its silver complex at pH 11.0. Experimental conditions: (A) 0.005% of (3a) solution against water blank; (B) the solution containing 2.0 μg ml^{-1} of Ag^+ and 0.015% of (3a) against the corresponding reagent blank.

Hence, (3a) was further evaluated for spectrophotometric determination of silver.

3.4.2. Effects of pH and (3a) concentration

The maximum absorbance for the color reaction of silver with (3a) was attained in the pH range 10.5–11.5. A pH of 11.0±0.2 was adopted and maintained with 0.03 mol l^{-1} Na_2HPO_4-NaOH buffer in this system. The optimum concentration range of 3a was found to be 0.01–0.02%, and 0.015% of (3a) was employed in this work.

3.4.3. Linearity

(3a) reacts rapidly with silver and the absorbance of the formed complex remains constant for at least 4 h. Beer's law is obeyed over the 0.08–7 μg ml^{-1} range of silver, and the linear regression equation is given by

$$A_{(\text{absorbance})} = 0.121C(\mu\text{g Ag}^+\ \text{ml}^{-1}) + 0.042,$$
$$n = 6,\ r = 0.982.$$

The detection limit (0.074 μg Ag^+ ml^{-1}) was defined as the concentration of silver which produces an absorbance equivalent to $3\sigma_b$, where σ_b is the standard deviation of the blank signal (n=12). Reproducibility tests (n=10) showed that the relative standard deviation of absorbance was 4.5% for 2 μg ml^{-1} of silver.

3.4.4. Effect of foreign species

The influence of many common species coexisting with silver was studied to establish possible interferences. The tolerable amount is that amount which gives a relative error of <±5% in analytical signal (absorbance) of the complex. For the determination of 20 μg Ag^+ in 10 ml of solution, the following ions do not interfere: 0.5 mg of Al(III) and Mg(II); 1.0 mg of Ca(II); 2.0 mg of K(I), Na(I), NO_3^- and PO_4^{3-}; 0.1 mg of Fe(III), Ti(IV) and Zn(II); 0.05 mg of Cr(III), Co(II), Cu(II), Fe(II) and Mn(II); 0.2 mg of SiO_3^{2-} and SO_4^{2-}.

3.4.5. Comparison with other methods

Compared to most of the reported spectrophotometric methods [25–28], the present one offers better selectivity for silver although its sensitivity is not so high. Such an improvement in selectivity may be attributed to the introduction of calixarene skeleton which has a strong binding ability toward Ag^+ [15]. Moreover, the proposed method can be directly employed in aqueous media, and does not need organic solvents or surfactants as other azocalixarenes do [13,15], due to the high solubility of (3a) in alkaline aqueous media. This makes the present system more simple.

4. Conclusions

In order to develop new spectroscopic calixarenes, especially chemiluminescent calixarenes, and improve their solubility in aqueous media, *p*-(2,3-dihydro-1,4-phthalazinedione-5-azo)calix[n]arenes (n=4, 6, 8) have been prepared by diazotizing luminol and then coupling with calix[n]arene. These new calixarenes show a multi-optical function, thanks to the presence of both phthalhydrazide and diazo groups. (3a) has been found to have not only a selective chromogenic response to Ag^+ but also an applicable chemiluminescent response to H_2O_2 with the help of catalyst Cu^{2+}. The good solubility of the prepared calixarene derivatives in aqueous media avoids the use of organic solvents or surfactants in the studied systems for silver or H_2O_2 determination.

Acknowledgements

Financial support of this work from the Alexander von Humboldt-Stiftung of Germany and NSFC is gratefully acknowledged.

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