Articles

An Effective Conductivity Amplifier and Computer Interfacing System for Chemical Kinetics

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A simple and reliable conductivity amplifier and a computer interfacing system for the chemical kinetics in solution are developed. They utilize the simplifications in circuit design offered by a function generator, operational amplifiers and true RMS to DC converter, and a 12 bit dual slope integrating analog-digital converter is interfaced to a personal computer through an 8255A programmable peripheral interface (PPI). It has a good sensitivity of 224 ppm and a low conductance drift of −200 ppm/℃ with temperature variation. In addition, a graphic computer software CCP(conductance checking program) which is capable of storing and analyzing conductance data for the first order kinetics is developed.

Introduction

A conductance measuring system is an important instrument in the chemistry laboratory. Such work relies on very precise determination of the conductance and a large body of literature has grown about the construction and use of conductivity cell and the measuring circuits.[1,2] Kinetic studies of reaction in solution may often by advantageous by measuring conductance change. The measurements can be achieved manually for a slow reaction for which measuring interval is longer than one minute, but the direct reading or data storing instruments are preferable for the faster reactions having shorter than a few seconds of measuring interval. Several direct reading circuits for the conductance measuring have been designed, and the most of these are based on a simple AC potential divider or the Wheatstone bridge.[3] However, an integrated circuit (IC) operational amplifier with a simple resistive input and feedback networks, Figure 1, has the following relation between input and output potentials:

$$E_o = -\frac{R_f}{R_i} E_i \tag{1}$$

provided the ratio R_f/R_i is very much less than the open-loop gain of the amplifier. The expression may be written as

$$E_o = -R_f\ G_i\ E_i \tag{2}$$

where G_i is the conductance of the input resistor.[4,5]

In practice, a purely resistive conductance cell can not be obtained, since a capacitance is arised in parallel from the finite area and separation of measuring electrodes, and a complex impedance is also arised in series from the electrolyte double layer at the surface of the electrode. More complete discussions of the impedance are given in the general texts[6]; it is sufficient to state here that it corresponds to quite a low impedance, and it only becomes important in highly conducting solution.[5] The introduction of the capacitance (C_i) increases the nonlinearity of response of the circuit to G_i, if the circuit is based on the Wheatstone bridge.[5] However, this is not serious for the operational amplifier circuitry. Again the electorytic double layer effects are ignored and Equation (4) describes the response of the circuit to the sinewave:[5]

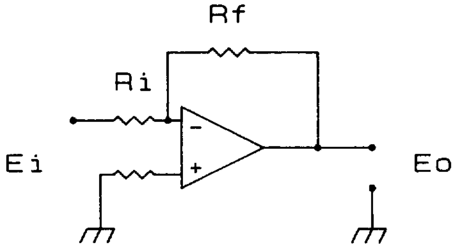


Figure 1. Operational amplifier conductance measuring circuit.

$$E_i = a\ \sin(\omega t) \tag{3}$$

$$E_o = -R_f\ G_i(1+R_i^2\ \omega^2\ C_i^2)^{1/2}\ a\ \sin(\omega t+\theta) \tag{4}$$

where $\tan\ \theta = R_i\ \omega\ C_i$

The equation (4) can be simplified as equation (2) by assuming that $R_i^2\ \omega^2\ C_i^2 \ll 1$, and this condition is always true in the measurement of chemical reactions of interest. Thus the desired linear relationship between the output potential and the conductance is very simply and precisely obtained for the operational amplifier. A sinewave or a squarewave is generally used as an exciting signal, but the choice between two types of signals is not so critical. Most of the conventional conductance meters consist of a sinewave generator, a feed back resistor network, its subsequent full wave rectifier

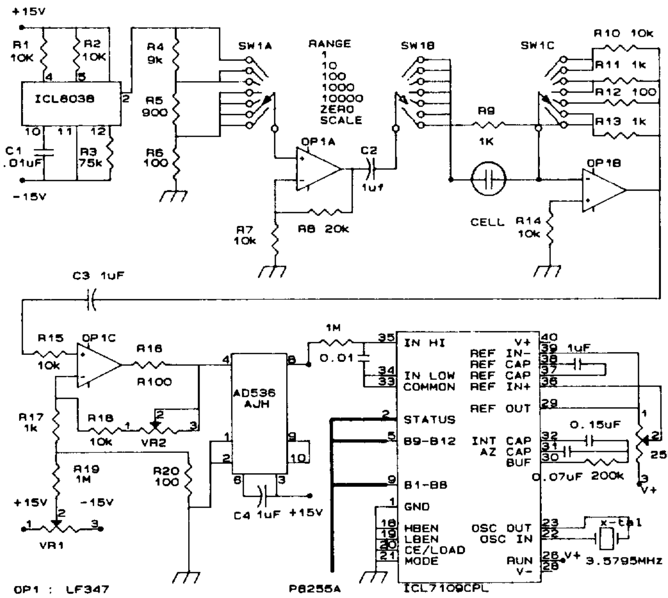


Figure 2. Schematic diagram of conductivity amplifier and A/D converter circuit. For clarity the standard power supply (+/− 15 V) and address decoding circuit have been omitted.

to get a pure DC signal, and a digital volt meter (DVM). However, it is not adequate for the faster reaction whose measuring interval is less than a minute or so because the response rate of the digital volt meter for the conventional conductance meter is not so fast. In addition, the conductance meter composed of a low resolution analog-digital converter makes large systematic error for the reaction where conductance change is small, and high conductance drift with temperature over long periods of time was monitored for some conventional conductance meters which we tested. It is for these reasons that we have designed a simple and reliable conductance amplifier with a computer interfacing system. It utilizes a function generator IC, a 12 bit binary analog-digital converter and the IBM PC bus interfacing,[7] though there is another type of interfacing, such as a serial communication through RS232C port. In addition, a graphic computer software which is capable of measuring, storing and analyzing conductance data for the first order kinetics, was written in Fortran and C language.

Hardware and Software

Conductivity amplifier. An overall circuit shown in Figure 2 is composed of a sinewave generator, a conductance amplifier, a gain or scaling amplifier, and a ture RMS-DC converter. A simple multivibrator circuit was usually constructed round one or two operational amplifiers, and is known as a two-phase oscillator, the Wein bridge oscillator and analogues. However, our preliminary circuit test shows that it is very difficult to limit amplitude of a exciting signal precisely and to get excellent temperature stability within a certain level of drift with zener diodes. Moreover, the Wein bridge oscillator with an automatic gain control (AGC) circuit has somewhat acceptable temperature stability, but has poor frequency stability. Again, it should be appended more parts which will affect the frequency stability and the distortion of a signal to construct the AGC circuit. Therefore, we used function generator IC (Intersil, ICL8038)[8] as an oscillator, and it showed very nice wave form with less distortion and good temperature stability.

The frequency was adjusted to 3.3 kHz sinewave by means of C1 and the amplitude of output signal was adjusted to 10 V peak to peak by OP1A and R8. The conductance amplifier is composed of OP1B and feed back resistor network R10-R13, and these resistors give conductance ranges covering 0.04-10^{-5} Ω^{-1}, which allow almost any conductance of chemical reactions of interest. The output of the OP1B is then connected to OP1C through C3 and is amplified properly by the OP1C and VR2 in order to measure it easily.

Off-set voltage of the OP1C was compensated by VR1. The output stage of the circuit is the ture RMS-DC converter (Analog Devices, AD536AJH), and the final DC signal is sent to a digital multimeter or to a computer through an analog to digital converter. Instead of using the ture RMS-DC converter, one can use a full-wave rectifier which is composed of a lot of additional parts such as a low pass filter.

The standard dual power supply(+/−15.0 volt) uses ICs 7815 and 7915, and the circuit has been omitted for clarity. The operational amplifier used in the circuit are all LF347 (quad) and ten-turn precision potentiometers are used to adjust off-set voltage and gain of the amplifier. High stability 1% metal film resistors are used in the overall circuit except feed back circuit, where 0.5% precision resistors are selected.

Analog-Digital circuit. A conversion circuit is shown in Figure 2 at the output stage of the RMS-DC converter AD536AJH, and is drawn only IC and some related parts.

The A/D conversion IC used in this application is the Intersil ICL7109CPL which is a 12 bit binary dual slope integrating converter and has a non-linearity of typically +/−0.2 counts and sensitivity of 244 ppm or $1/(2^{12}-1)$. Also, ICL7109 is a high performance converter designed to interface easily with microprocessors. Full scale or analog input voltage is adjustable between 409.6 mV to 4.096 V by means of some parts and we have fixed to 4.000 V in this application. A frequency of a crystal oscillator will determine the integrating rate, *i.e.*, measuring interval, and the 3.5795 MHz is adopted in order to reject noise due to 60 Hz power supply. With parts shown in Figure 2, eight conversions per second is possible, but one can easily expand to 30 conversions per second by replacing some parts, such as crystal oscillator and an integrating capacitor (INT CAP). For optimum performance of the converter, care must be taken in the selection of values for the capacitors and resistors. Here we used polypropylene capacitors for low leakage characteristics and also 1% metal film resistors. To send digital signal from the converter to the computer, we adopted direct mode where the MODE pin of the ICL7109 is left at low level, and RUN/HOLD is left at high level always. This interface means read-anytime mode and timing problem will be avoided by reading STATUS output as well.[8] The Intel 8255A PPI (programmable peripherial Interface) which is a general purpose I/O device designed for use with the Intel CPU, was used to interface with a microprocessor. For convenience, a ready made IBM PC/XT/AT prototype card[9] which has an address decorder and a counter, and it utilized programmable logic

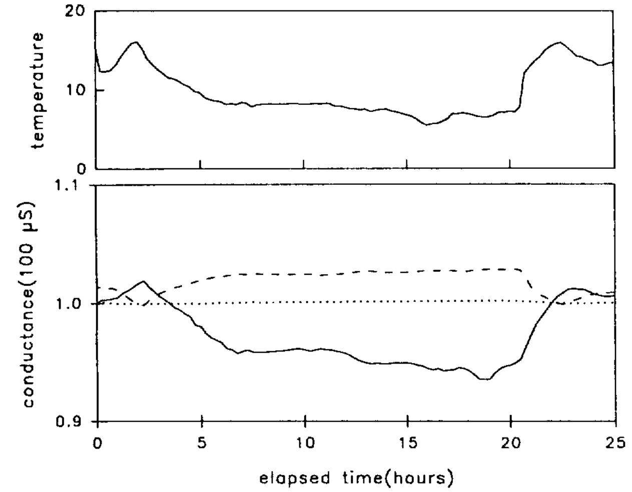


Figure 3. Temperature stability of conductivity amplifier over a long period of time. solid line: amplifier with two-phase oscillator; dotted line: amplifier with ICL8038 sinewave generator; dashed line: SUNTEX model SCX-17A.

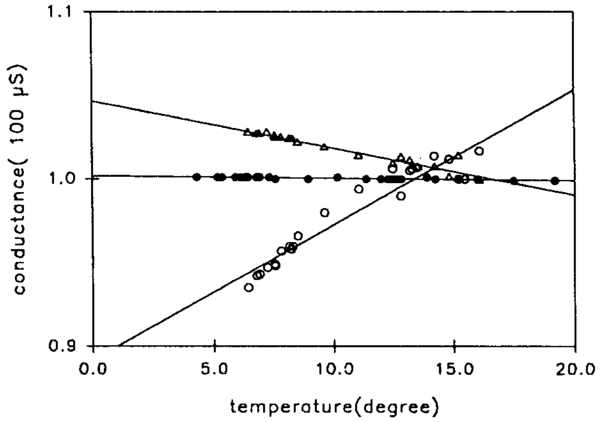


Figure 4. Temperature stability of conductivity amplifier with 1% metallized film resistor (1 k ohm). (○): amplifier with two-phase oscillator: (●): amplifier with ICL8038 sinewave generator; (△): SUNTEX model SCX-17A.

device (PLD) PAL20V8 to get a maximum flexibility in configuring of the address of the device. The address of the device can be a value between 240H and 3FFFH, and this can remove address jam with existing cards.

Software. A software package consist of the programs for measuring and storing the DC potential obtained by the conductance amplifier, a program for editing, and a nonlinear regression program to determine the first order rate constants. The graphic main program which is called CCP (conductance checking program) is written in C language, and the others are written in Fortran. The main program adopted pull-down menu structure, and the primary menu consists of Tool, System, Run, Option, and Program. Zero and gain adjustments are performed in option Tool, and editing a file and DOS Shell command are performed in option System. The option Run controls overall program, and the preliminary works such as defining measuring interval, file name to store conductance data, and mixing time for the fast reaction are specified at menu Option. Sometimes one may encounter certain difficulty arising in injecting a sample and executing the program simultaneously. To overcome such a problem, a warning signal will ring to notify on time to inject. At menu Program, the regression program or the other statistical package may be used to analyze raw data. All program can run under the Intel 8086-80486 based on DOS operating system with less than 400KB memory and a monochrome or color monitor. Editing raw data can be done through two types of modules; the first one is a general text editor which any user favors, and the other one is special program named LSKED which is combined with the regression program we will disscuss below. In the program LSKED, one may omit some data which have a large standard deviation obtained from the first cycle of regression in order to get better rate constant with smaller standard deviation. This treatment is similar to assigning automatic weighting factor. The non-linear regression program, LSK which is for the main frame computer and has been written by Bentley *et al.*[10] was converted to use at the PC level. This program can be used as a separate program and/or can be called from the PROGRAM at the main program. The text editor can be varied by users, and any kind of the program may be registered to the main program for maximum convenience.

Performance. The wave form of each circuit block was confirmed by an oscilloscope and there were no measurable amount of distortion and noise. The off-set potential of the operational amplifier did not change much over a long period of time, and the chassis-mounted 10 turn potentiometer was replaced by one for the printed circuit board(PCB). This reduces some external adjustment knobs. To check thermal stability, three kinds of conductivity amplifiers were tested; conventional conductivity meter SUNTEX model SCX-17A, the meter constructed with a two phase oscillator, and the meter constructed for this work. The data storage multimeter, Keithley model 193, which has the resolution of $6\frac{1}{2}$ digit was used to trace the conductance variance with temperature change of the laboratory for longer than one day. The signal given by a high stability resistor connected across the cell terminal was monitored. The results are shown in Figures 3 and 4 for the temperature range of 5-20℃. From the slope of these figures, the conductance drift with temperature was −2800 ppm/℃, 8100 ppm/℃, and −200 ppm/℃ for the SUNTEX SCX-17A, the meter with conventional two phase oscillator, and the instrument made in this work, respectively. The large conductance drift with temperature variation of the former two types of the conductance meter is due to the oscillator circuit, and the major part which affect conductance drift is input alternate current(AC) that is applied at the inversion amplifier of the OP1B. Therefore one can enhance the stability of the conductance meter by the replacement of an oscillator circuit. Based on this small drift, the sensitivity of the conductance amplifier we made is within 244 ppm which is that of the analog to digital converter itself.

A reference DC potential generator composed of a precision 10 turn potentiometer and a dry cell has been used to test linearity and results are shown in Figure 5. The least squares analysis of the line shows excellent linearity with

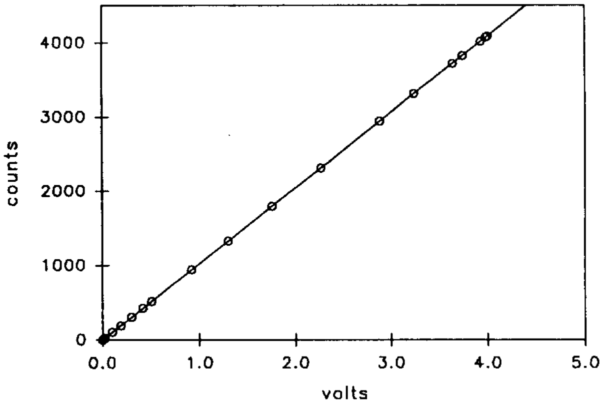


Figure 5. A/D converted values of known DC potential.

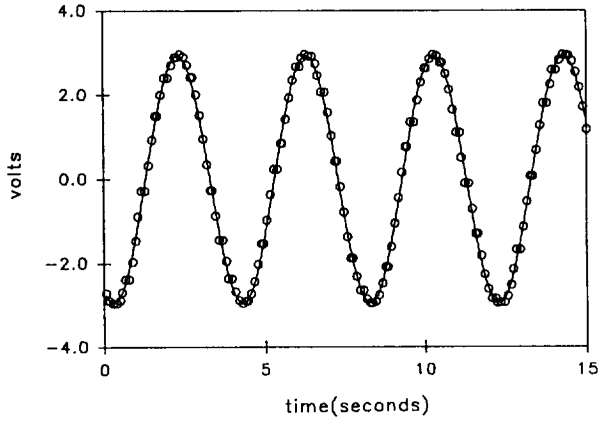
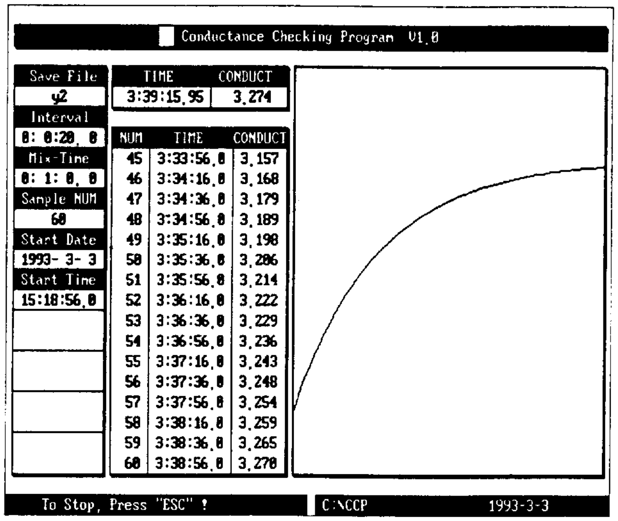


Figure 6. Trace of 0.250 Hz sinewave obtained by A/D converter

correlation coefficients of 1.000 over the full range, and it was saturated at 4.005 volts.

To test the response rate, 0.250 Hz sinewave(period : 4 seconds) which was generated by the precision function generator was traced by the converter, and the data were collected for 15 seconds neither specifing measuring interval nor reading STATUS output. In Figure 6 each point represents observed potential and the solid line represents curve fitted results by the equation of a sinewave. The duplicated points represent that previous value remains in data latch while a subsequent conversion is doing because the converter works as a read-anytime mode.[8] From these results, it is clear that seven or eight conversions per second is readily achieved. Though the slowest part of the instrument is the RMS-DC converter, it did not make any problem because the conversion rate of this IC is 25 ms or 40 conversions per second. Thus it is suitable for the reactions with a turbo conductance cell in which measuring interval is about 0.2 seconds, *i.e.*, 5 or 6 conversions per second. To follow faster reaction, one should use a flow cell and adjust the frequency of the crystal oscillator. The whole system including the software was tested for the reactions with known rate constant. The Figure 7 shows the screen of CCP performed at menu RUN. The reaction is for the solvolyses of furoyl chloride of 20% methanol-water mixed solution at 25℃. The rate constant of the reaction is 3.10×10^{-3} s^{-1} and the other constants were summarized at the previous works[11].



Save File
y2
Interval
0: 0:20. 0
Mix-Time
0: 1: 0. 0
Sample NUM
60
Start Date
1993- 3- 3
Start Time
15:18:56.0

TIME	CONDUCT
3:39:15.95	3.274

NUM	TIME	CONDUCT
45	3:33:56.0	3.157
46	3:34:16.0	3.168
47	3:34:36.0	3.179
48	3:34:56.0	3.189
49	3:35:16.0	3.198
50	3:35:36.0	3.206
51	3:35:56.0	3.214
52	3:36:16.0	3.222
53	3:36:36.0	3.229
54	3:36:56.0	3.236
55	3:37:16.0	3.243
56	3:37:36.0	3.248
57	3:37:56.0	3.254
58	3:38:16.0	3.259
59	3:38:36.0	3.265
60	3:38:56.0	3.270

To Stop, Press "ESC" !

C:\CCP 1993-3-3

Figure 7. Main view of program CCP with option RUN.

Conclusion

A simple and reliable conductance amplifier which is composed of a function generator IC, OP amps and a true RMS-DC converter has been constructed, and it has also been interfaced to the personal computer through PC bus and a 12 bit dual slope analog-digital converter.

It has been known that the conductance drift for the conventional instrument with the temperature change was caused by the instability of the sinewave oscillator, and such a drift has been removed by using the function generator IC. With this integrated circuit, the conductance amplifier has the drift coefficient of −200 ppm/℃.

The analog-digital converter has good sensitivity of 224 ppm and also gives good linearity over a full range. In addition to the amplifier, a graphic software package which is composed of modules for measuring, storing, and analyzing conductance data was also developed to determine rate constants for the reactions with half-lives from a second to several days.

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Selective Nitration of Calix[4]arene

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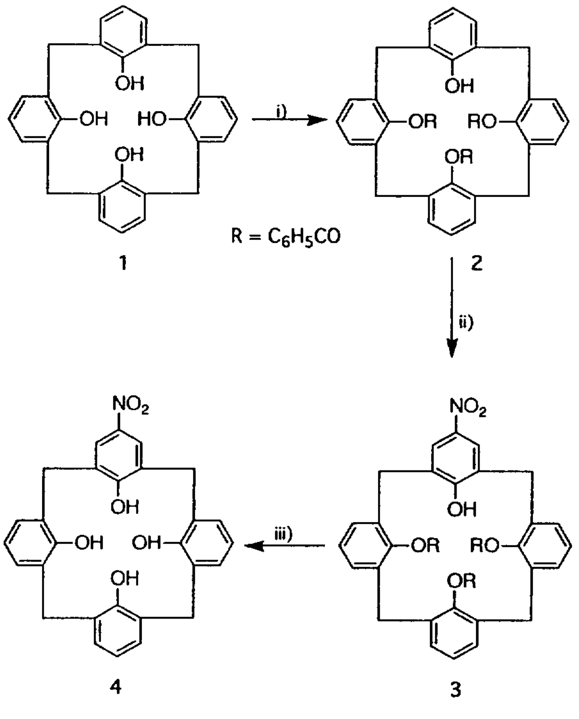
Mono and 1,3-dinitrocalix[4]arene **4** and **7** were prepared by the selective benzoylation followed by nitration. Benzoylation of calix[4]arene with benzoyl chloride in the presence of pyridine produced the tribenzoyl and 1,3-dibenzoyl-calix[4]arene selectively depending on the reaction conditions. Nitration of tribenzoyl and 1,3-dibenzoyl-calix[4]arene was conducted with nitric acid in the presence of acetic acid to produce mono and 1,3-dinitrocalix[4]arene. Removal of benzoyl groups was carried out with NaOH in ethanol to give **4** and **7**.

Introduction

Calixarenes[1] are cavity containing metacyclophanes which can complex with various guest compounds. Functional groups can be introduced by the utilization of upper rim[2,3] and lower rim[4] of calix[4]arene. Nitro groups can be introduced on the upper rim of calix[4]arene developed by Shinkai[5] and K. H. No method[6]. Nitrocalixarenes show a very strong acidic protons[7] which may be utilized on the catalytic reaction as well as a proton sensor. But they introduced the nitro groups to the all four para position of calixarene.

Selective nitration of calixarene was reported by Bohmer[8] and Reinhoudt[9]. Bohmer's group synthesized mononitrocalix[4]arene *via* step-wise methods. Reinhoudt group reported the synthesis of 1,3-dinitrocalix[4]arene but succeeded only on O-dimethylated calix[4]arene which could not show the strong acidity.

We report here the synthesis of two nitro-calix[4]arenes including mononitrocalix[4]arene **4**, and 1,3-dinitrocalix[4]arene **7**. Direct nitration of calix[4]arene with nitric acid fail to introduce the selective nitro groups to the para position of calix[4]arene. To introduce the nitro groups to the calix[4]arene selectively we utilized the differences of reactivity for the nitration of phenol ring depending on the substituents on hydroxy group with benzoylation. Selective benzoylation of calix[4]arene developed by Gutsche[10], and Nam[11] groups could provide the best candidate for the synthesis of selective nitrocalix[4]arene. Benzoyl group not only can deactivate the nitration reaction of calix[4]arene but also can be easily removed by the hydrolysis with base[10].



i) Excess benzoyl chloride in pyridine
ii) 1 equivalent of nitric acid (70%) at room temperature
iii) Refluxing with NaOH in EtOH

Figure 1. Synthesis of Mononitrocalix[4]arene.

Mononitrocalix[4]arene **4** was prepared from tribenzoylcalix[4]arene[10] **2** by the reaction of nitration followed by hydrolysis as shown in Figure 1. Calix[4]arene **1** was treated with excess benzoyl chloride in pyridine under ice bath to yield the tribenzoylated calix[4]arene **2**. Nitration was conducted with the treatment with 70% nitric acid in the pres-