A New Resonance Light Scattering Method to Determine Quercetin

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Summary: The paper established a new resonance light scattering method for determining quercetin content in water solution. It was found that in hexamine buffer solution (pH7.50), sodium-dodecyl-benzene-sulfonate-hexadecyl-trimethyl-ammonium-bromide system can enhance the resonance light scattering intensity of quercetin which is in proportion to the content of quercetin in the range of 2.0×10^{-9} to 5.0×10^{-5}mol/L. The detection limit is 5.0×10^{-10}mol/L.

Keywords: quercetin, sodium-dodecyl-benzene-sulfonate, hexadecyl-trimethyl-ammonium-bromide, resonance light scattering

Introduction

Quercetin (Fig. 1) is one of the most important flavonoid found in many herbs and fruits [1-3] and has many physiological activities. Quercetin can maintain resistance of blood vessels [4], reduce their osmosis and brittleness. In addition, quercetin was found to inhibit growth of leukemia cells [5-7], Ehrlich [8] and Nemeth-Kellner Lymphoma [9] ascites tumor cells. Several studies shown quercetin may have anti-inflammatory properties [10-11] and affect certain mechanisms of cancer[12-13], and it is being investigated for a wide range of potential health benefits [12-14]. In 2007, a study [15] shown that quercetin displayed inhibition against HIV-1 reverse transcriptase. Therefore quercetin has been used for clinical treatment [16-19]. The quantitative analysis of quercetin is important for the control medicine and the test of therapy effects. The familiar methods of analyzing quercetin are spectrophotometry [20-21], pulse polarography [22], electrochemical [23], HPLC [24-25] methods. But the pulse polarography and chromatography have the drawback of manipulation step complex and instrument expensive which restricts the application. The resonance light scattering analysis method was applied in analytical chemical especially biochemistry due to high sensitivity and selectivity [26-29]. Herein, it was found that the resonance light scattering intensity of quercetin was greatly enhanced by sodium-dodecyl-benzene-sulfonate-hexadecyl-trimethyl-ammonium-bromide mixed micelle and a resonance light scattering analysis method for determining quercetin was proposed. The interaction mechanism was discussed.

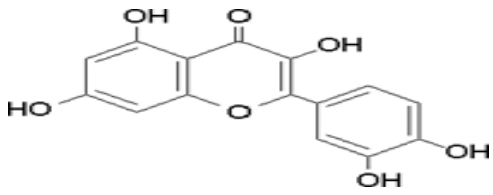

Fig. 1: Chemical structure of quercetin

Results and discussion

The resonance light scattering (RLS) spectra of quercetin(Qu), Qu-sodium-dodecyl-benzene-sulfonate (SDBS), Qu-hexadecyl-trimethyl-ammonium-bromide (CTMAB), SDBS, CTMAB and Qu-SDBS-CTMAB systems were shown in Fig. 2 which indicated that RLS intensity of Qu can be greatly enhanced by addition of SDBS-CTMAB. Furthermore, the RLS intensity of Qu-SDBS-CTMAB was larger than that Qu-SDBS and Qu-CTMAB which indicated that there was interaction between Qu and SDBS-CTMAB.

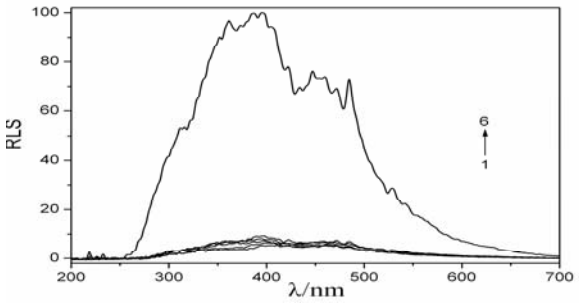

Fig. 2: RLS spectra: 1. Qu, 2. Qu-SDBS, 3. Qu-CTAB, 4. SDBS, 5. "CTAB", 6. Qu-SDBS-"CTMAB" Conditions, Qu 1.0×10^{-6}mol/L, SDBS 1.0×10^{-3}mol/L, CTMAB 1.0×10^{-3}mol/L, HMTA 5.0%, pH7.50

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Experimental

Chemicals

Unless otherwise noted, all reagents and solvents used in this study were analytical grade obtained from Chemical Company of China (Shanghai, China). A 10% hexamine buffer solution (HMTA) was adjusted to pH value 7.50 with HCl using a Delta 320-S acidity meter (Mettler Toledo, Shanghai, China). A Qu stock solution was prepared by dissolving Qu in ethanol. The SDBS and CTMAB stock solution were prepared by dissolving the corresponding reagents in distilled water.

Method

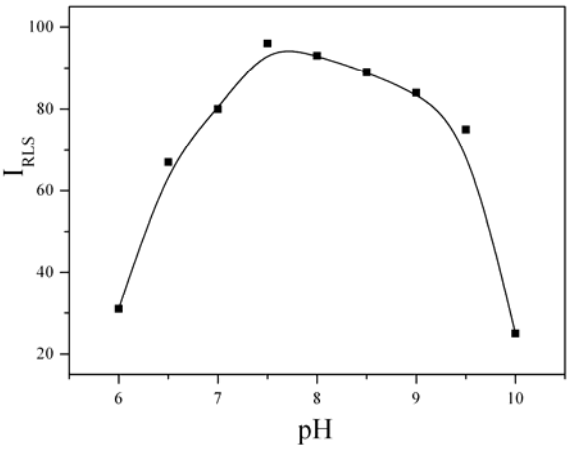
RLS spectra were recorded with a LS-55 spectrofluorimeter (Perkin-Elmer, USA) in a 1-cm quartz cuvette (Perkin-Elmer, USA). Critical micelle concentration (CMC) data were measured on a processor tensiometer-K12 (with a precision of $0.01 mNm^{-1}$, Krüss, Hamburg, Germany) by the Wilhelmy plate (Krüss, Hamburg, Germany). Ultraviolet-visible (UV-vis) spectra were recorded on a UV-2450 spectrophotometer (Shimadzu, Tokyo, Japan) at room temperature in a 1-cm quartz cuvette (Shimadzu, Tokyo, Japan).

Procedure

The required amount of solutions was successively added in the following order, HMTA, Qu, SDBS and CTMAB. The mixture was diluted with water and mixed thoroughly, then measured after 20 minutes. All RLS spectra were obtained by scanning simultaneously excitation and emission monochromators ($\Delta\lambda$=0nm) from 200 to 700 nm. RLS intensity was measured at λ = 396.0 nm in a 1.00 cm quartz fluorescence cell.

Effect of Buffer Solution and pH Value

Effect of pH value on RLS intensity of Qu was shown in Fig. 3 which indicated the maximum RLS intensity was obtained in pH value 7.50. RLS intensity for Qu in HMTA-HCl, NH_4Cl-NH_3, tris-HCl, NaH_2PO_4-citric acid, sodium diethylbarbiturate-HCl, NaH_2PO_4-Na_2HPO_4 and borax-boracic acid buffer solution was 100, 80.3, 82.0, 79.0, 50.3, 20.1 and 10.1,(SDS)respectively, which illuminated that HMTA-HCl was the most suitable buffer solution. Further studies demonstrated the optimal concentration of HMTA was 5.0 %.



Conditions, Qu 1.0×10^{-6}mol/L, SDBS 1.0×10^{-3}mol/L, CTMAB 1.0×10^{-3}mol/L, HMTA: 5.0%

Fig. 3: I_{RLS} of Qu versus pH value.

Effect of Surfactants

Different surfactants had different influences on RLS intensity of Qu. Table-1 clearly showed that in the mixed surfactants of SDBS-CTMAB, Qu had the greatest RLS intensity.

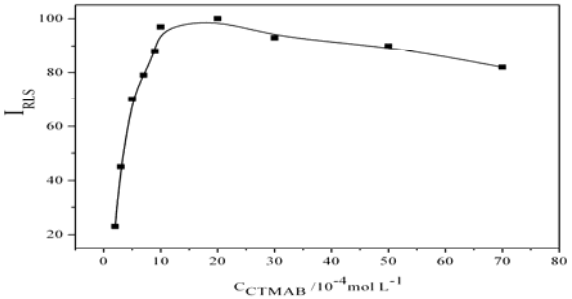
Table-1: Effect of surfactants

surfactants	I_{RLS}□%□	surfactants	I_{RLS}□%□
No surfactants	**5.3**	**Tx100**	**3.7**
SDBS	**6.4**	**SDBS+Tx100**	**4.0**
CTMAB	**7.3**	**SDS+CTMAB**	**5.5**
SDBS+CTMAB	**100**	**SDS+Tx100**	**1.5**
SDS	**2.3**		

Conditions, Qu 1.0×10^{-6}mol/L, pH7.50, HMTA 5.0%, SDBS 1.0×10^{-3}mol/L, CTMAB 1.0×10^{-3}mol/L, SDS 1.0×10^{-3}mol/L, Tx100 1.0×10^{-3}mol/L

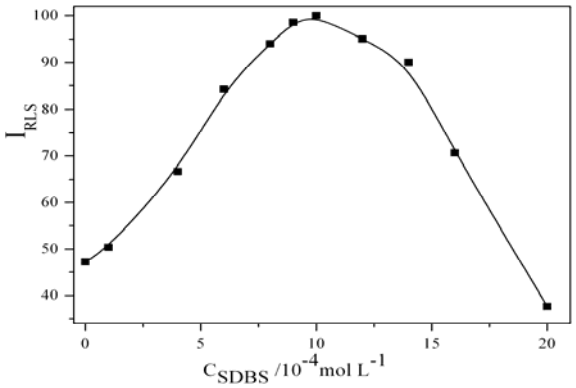
Effect of SDBS and CTMAB

Fig (4, 5) indicated that the optimal concentration of both SDBS and CTMAB was 1.0×10^{-3}mol/L.



Conditions, Qu 1.0×10^{-6}mol/L, SDBS 1.0×10^{-3}mol/L, pH7.50, HMTA 5.0%

Fig. 4: I_{RLS} of Qu versus concentration of CTMAB.



Conditions, Qu 1.0×10^{-6}mol/L, CTMAB 1.0×10^{-3}mol/L, pH7.50, HMTA 5.0%

Fig. 5: I_{RLS} of Qu versus concentration of SDBS.

Addition Order and Time Evolution Effects

Effect of addition order was tested and results indicated that the optimum addition order was HMTA, Qu, SDBS and CTMAB. Effect of time evolution was studied which showed that RLS intensity reached a maximum after 20 min and remained stable for over 2h. Therefore, this system exhibited good stability.

Foreign Substances Effect

Interference of foreign substances was tested and shown in Table-2. It was found that most of ions had little effect on the determination of 1.0×10^{-7}mol/L Qu within the permissible ±5% error.

Table-2: Effect of foreign substances

Foreign substances	Concentration (1.0×10^{-7}mol/l)	ΔI_{RLS} (%)
Fe^{3+}, Cl^-	200	-2.1
Al^{3+}, Cl^-	180	-4.8
Mn^{2+}, Cl^-	360	-1.5
Ba^{2+}, Cl^-	200	-2.6
Na^+, CO_3^{2-}	3100	-2.3
Eu^{3+}, Cl^-	120	-3.1
Tb^{3+}, Cl^-	150	-2.2
K^+, Cl^-	6300	-1.0
Na^+, $H_2PO_4^-$	1000	-2.3

Conditions, Qu 1.0×10^{-7}mol/L, SDBS 1.0×10^{-3}mol/L, CTMAB 1.0×10^{-3}mol/L, HMTA 5.0%, pH7.50

Analytical Applications

Calibration Graphs

Under optimum condition defined, the calibration graph for Qu was obtained and shown in Table-3. It can be seen that there was a linear relationship between RLS intensity and Qu concentration in the range of 2.0×10^{-9}-5.0×10^{-5}mol/L. The detection limit (S/N=3) was 0.5nmol/L.

Table-3 Analytical parameters

	Linear range (mol/L)	Linear regression equation (mol/L)	Correlation coefficient	Detection limit (nmol/L)
Qu	2.0×10^{-9}-5.0×10^{-5}	$I_{RLS}=1.3\times10^7C+2.82$	0.999	0.5

Conditions SDBS 1.0×10^{-3}mol/L, CTMAB 1.0×10^{-3}mol/L, HMTA 5.0%, pH7.50

Samples Determination

Table-4: Determination of Qu in synthetic samples

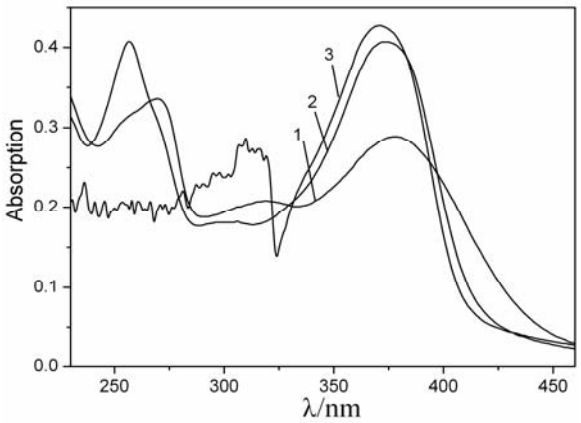
sample	coexisting substance	sample added (10^{-6}mol/L)	sample founded (10^{-6}mol/L)	Recovery (%)	RSD (%)
Qu	Fe^{3+}, Al^{3+}, Mn^{2+} Na^+, Y^{3+}	2.0	1.98	99	2.5

Conditions, SDBS 1.0×10^{-3}mol/L, CTMAB 1.0×10^{-3}mol/L, HMTA 5.0%, pH7.50

To test the method, the content of Qu in synthetic samples containing metal ions according to results shown in Table-4 was determined. The standard addition method was used for the determination of Qu. From Table-4, it can be seen that Qu in synthetic sample can be determined with satisfactory results.

Mechanisms

Absorption Spectra

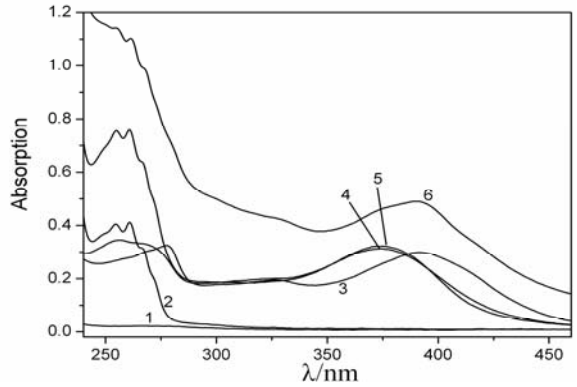


1. Qu-H_2O, 2. Qu-ethanol, 3. Qu-acetone Conditions, Qu 5.0×10^{-5}mol/L

Fig. 6: Absorption spectra.

From Fig. 2, it was shown that Qu-SDBS-CTMAB system had the RLS band of 300-500 nm. Fig (6 and 7) indicated that Qu had two characteristic

absorption peaks of 255nm and 375nm, which corresponded to the transition of n→π* (benzoyl peroxide chromophore) and π→π* cinnamic acid chromophore), respectively [30-33], whereas SDBS and CTMAB had not absorption in 300-500nm. The facts demonstrated that the RLS of Qu-SDBS-CTMAB system was due to Qu absorption rather than SDBS and CTMAB.



1. CTMAB, 2. SDBS, 3. Qu, 4. Qu-CTMAB, 5. Qu-SDBS, 6. Qu-CTMAB-SDBS
Conditions, Qu 5.0×10^{-5}mol/L, SDBS 1.0×10^{-3}mol/L, CTMAB 1.0×10^{-3}mol/L, HMTA 5.0%, pH7.50

Fig. 7: Absorption spectra.

Formation of Qu-CTMAB-SDBS complex

Fig. 2 shown that the RLS intensity of Qu-CTAMB-SDBS system was strong than Qu, Qu-SDBS, Qu-CTAB, SDBS, CTMAB systems, which indicated it was possible that the large complex Qu-SDBS-CTMAB was formed.

RLS Enhancing Effect

To research the microenvironment offered by mixed micelle, the absorption spectra of Qu in water, ethanol and acetone was studied. From Fig. 6, it can be seen the absorption intensity of 375nm enhanced upon the reduction of solvent polarity (H_2O□ethanol□acetone) which indicated that small solvent polarity can offer optimal microenvironment for the absorption. The solvent polarity of mixed micelle was less than SDBS and CTMAB solution which induced the absorption of Qu enhanced. It was possible that Qu can come into the cavity of mixed micelle and form mixed micelle inclusion which resulting in absorption intensity of Qu enhanced and the absorption peaks shifted [34] and the result was the enhancement of RLS of Qu.

Conclusions

In this paper, a new sensitive RLS method for the determination of Qu was reported. Under optimum conditions, the RLS intensity was in proportion to Qu concentration in the range of 2.0×10^{-9}-5.0×10^{-5}mol/L. The detection limits (S/N=3) was 0.5nmol/L.

Acknowledgements

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