Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPOTING INFORMATION

Probing the Temperature Dependent Changes of the Interfacial Hydration and Viscosity of Tween20:Cholesterol(1:1) Niosome Membrane using Fisetin as Fluorescent Molecular Probe

Jhili Mishra, Jitendriya Swain and Ashok Kumar Mishra*

mishra@iitm.ac.in

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India

Figure S1. Uv-visible absorption spectra of fisetin in TW20 micelle. The increase in absorbance value with increase in TW20 concentration indicates the solubilization of fisetin in TW20 micelle. [Fisetin] = 5μM

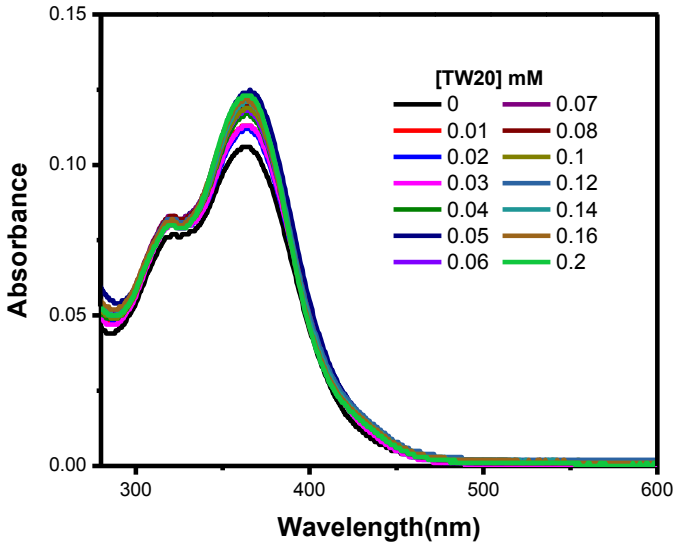

Figure S2. (A) Emission spectra of fisetin in TW20 micelle**.** The emission intensity increases with increase in TW20 concentration as the process of micellization start. **(B)** Plot for the variation of fisetin tautomer emission maximum (cm^{-1}) with variation in TW20 concentration. Point of inclination gives the critical micellar concentration (CMC) value of TW20. **(C)** Plot for the fluorescence intensity ratio ($I_{Tautomer}/I_{Anion}$) of fisetin in TW20 micelle. Intensity ratio plot indicates that the hydrophobicity of the TW20 micellar medium increases with increase in TW20 concentration. [Fisetin] = 5μM, λ_{ex} = 370 nm, slit width = 5/5 nm

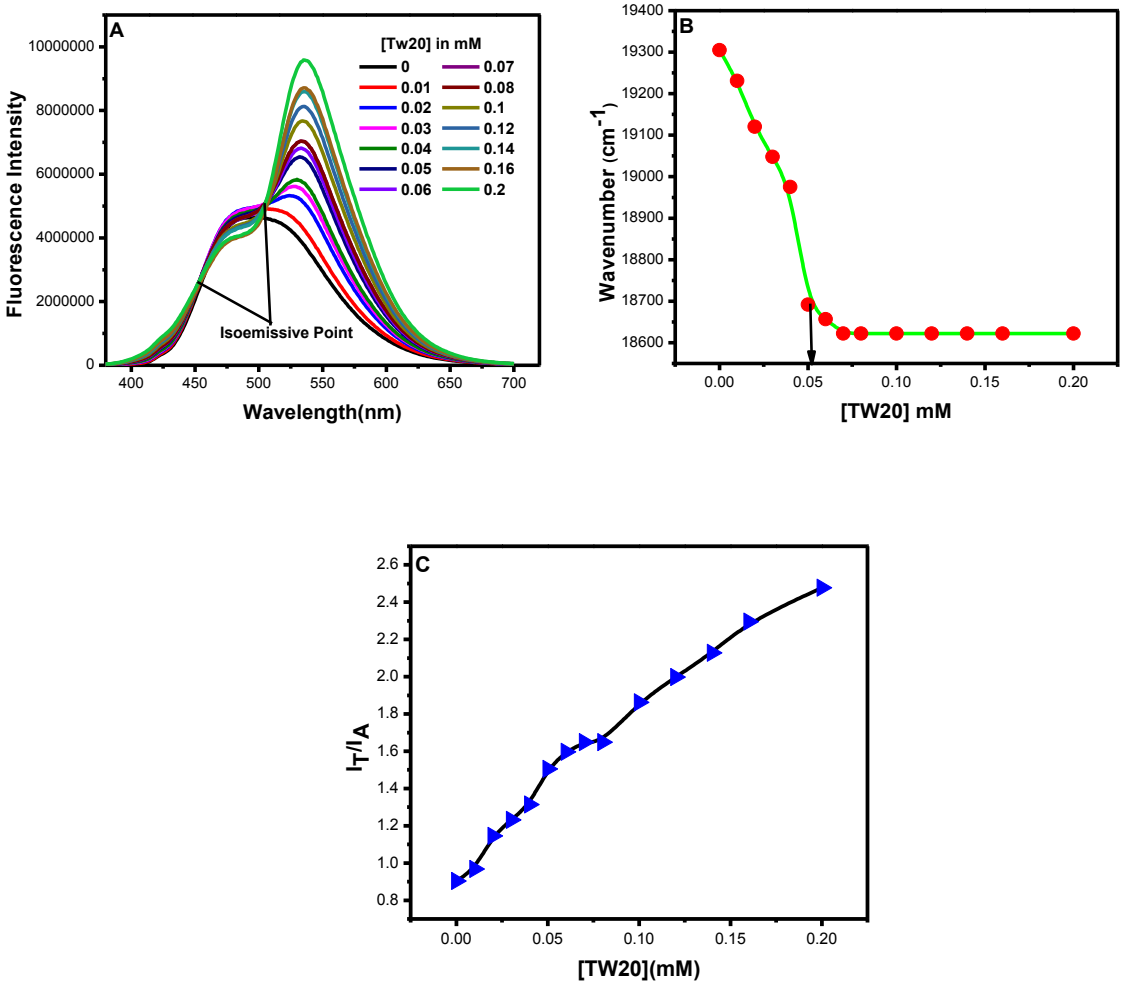

Figure S3. Fluorescence Anisotropy plot for phototautomer emission of fisetin in TW20 micelle. The increase value of anisotropy indicates that the rigidity of the medium increases with increase in TW20 concentration. [Fisetin] = 5μM**,** λ_{ex} = 370 *nm*, λ_{em} = 535 *nm*

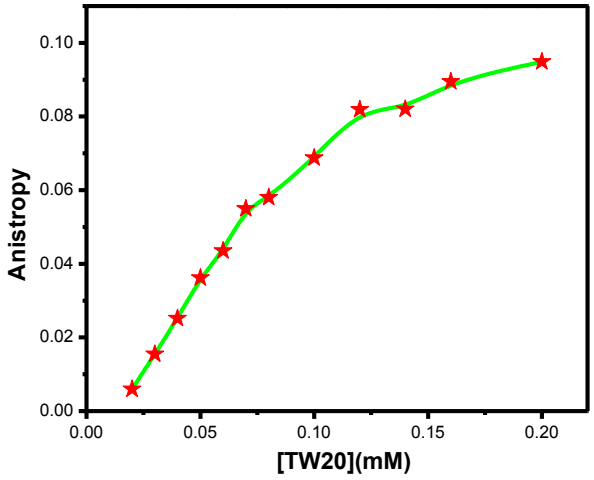

Figure S4. The fluorescence lifetime decay of Anionic emission of fisetin in TW20 micelle. [Fisetin] = 5μM, λ_{ex} = 370 *nm*, λ_{em}=490 *nm*.

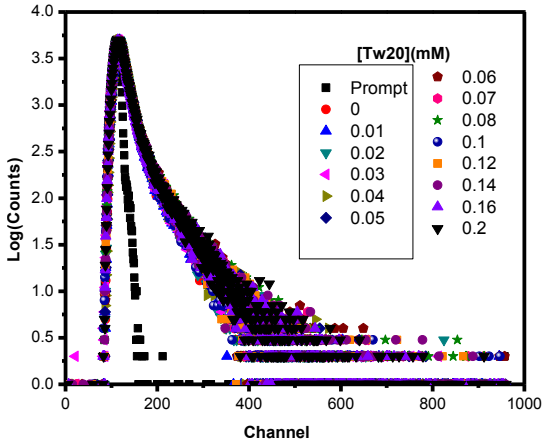

Table S1. Fluorescence lifetime data (nanosecond) of anionic emission of fisetin in TW20 micelle. λ_{ex} = 370 *nm*, λ_{em}= 490 *nm*. [Fisetin] = 5μM, Error = ± 5%

[Tw20] mM	τ1,(α1)	τ2,(α2)	B1	B2	χ2
0	$0.8_6(83)$	$3.4_1(17)$	0.94	0.05	1.09
0.01	$0.8_7(83)$	$3.3_{6(}17)$	0.95	0.04	1.11
0.02	$0.8_6(82)$	$3.3_4(18)$	0.94	0.05	1.19
0.03	$0.8_8(83)$	$3.5_3(17)$	0.95	0.04	1.05
0.04	$0.8_7(83)$	$3.3_3(17)$	0.94	0.05	1.02
0.05	$0.8_8(80)$	$3.4_7(20)$	0.94	0.05	0.99
0.06	$0.8_6(79)$	$3.3_8(21)$	0.94	0.05	1.05
0.07	$0.8_7(80)$	$3.4_5(20)$	0.94	0.05	1.01
0.08	$0.8_8(78)$	$3.5_0(22)$	0.94	0.05	1.00
0.1	$0.8_4(81)$	$3.2_0(20)$	0.94	0.05	1.14
0.12	$0.8_{8(}78)$	$3.3_9(20)$	0.93	0.06	1.01
0.14	$0.8_8(80)$	$3.5_4(20)$	0.93	0.06	1.03
0.16	$0.8_6(80)$	$3.3_8(20)$	0.94	0.05	1.19
0.2	$0.8_8(79)$	$3.4_9(21)$	0.93	0.06	1.06

Figure S5. The fluorescence lifetime decay of tautomeric emission of fisetin in TW20 micelle. λ_{ex} = 370 *nm*, λ_{em}=535 *nm*, .[Fisetin] = 5 μM

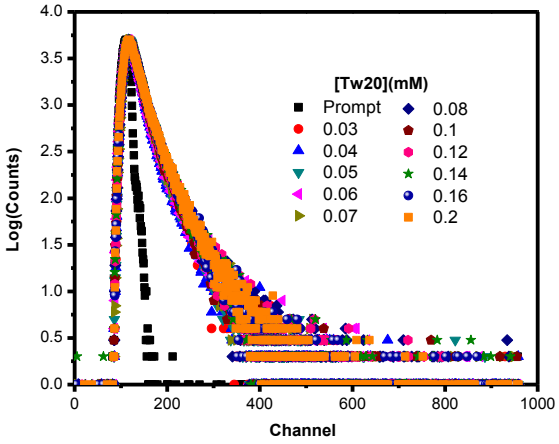

Table S2. Fluorescence lifetime data (nanosecond) of tautomeric emission of fisetin in Tw20 micelle. λ_{ex} = 370 *nm*, λ_{em}= 535 *nm*.[Fisetin] = 5μM, Error = ± 5%

[tw20]	τ1,(α1)	τ2,(α2)	B1	B2	χ2
0.03	$1.0_4(86)$	$3.0_1(14)$	0.94	0.05	1.09
0.04	$1.0_5(88)$	$3.1_7(12)$	0.95	0.04	1.14
0.05	$1.0_8(86)$	$3.1_4(14)$	0.94	0.05	1.01
0.06	$1.1_1(86)$	$3.2_7(14)$	0.94	0.05	1.16
0.07	$1.1_2(84)$	$3.0_9(16)$	0.93	0.06	1.08
0.08	$1.1_8(81)$	$2.9_6(19)$	0.91	0.08	1.06
0.1	$1.1_8(85)$	$3.0_4(15)$	0.93	0.06	1.16
0.12	$1.2_1(84)$	$3.1_0(16)$	0.93	0.06	1.16
0.14	$1.2_3(82)$	$2.9_5(18)$	0.93	0.08	1.05
0.16	$1.2_0(81)$	$2.9_0(19)$	0.91	0.08	1.02
0.2	$1.3_2(86)$	$3.2_4(14)$	0.93	0.06	1.22

$$Y = Y_{\max} \frac{[Fisetin]}{K_d + [Fisetin]} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (i)$$

$$\frac{1}{Y} = \frac{K_d + [Fisetin]}{Y_{\max}[Fisetin]} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (ii)$$

$$\frac{1}{Y} = \frac{K_d}{Y_{\max}[Fisetin]} + \frac{[Fisetin]}{Y_{\max}[Fisetin]} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (iii)$$

$$\frac{1}{Y} = \frac{K_d}{Y_{\max}[Fisetin]} + \frac{1}{Y_{\max}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (iv)$$

$$\underbrace{\frac{1}{Y}}_{y} = \underbrace{\frac{K_d}{Y_{\max}[Fisetin]}}_{mx} + \underbrace{\frac{1}{Y_{\max}}}_{c}$$

Scheme S1. Simplified form of equation 6(partition coefficient calculation)

Figure S6. Emission spectra of fisetin in TW20:cholesterol(1:1) niosomes with increasing fisetin concentration at higher temperature (60 ^{o}C). λ_{ex} = 370 *nm*, slit width = 5/5 nm

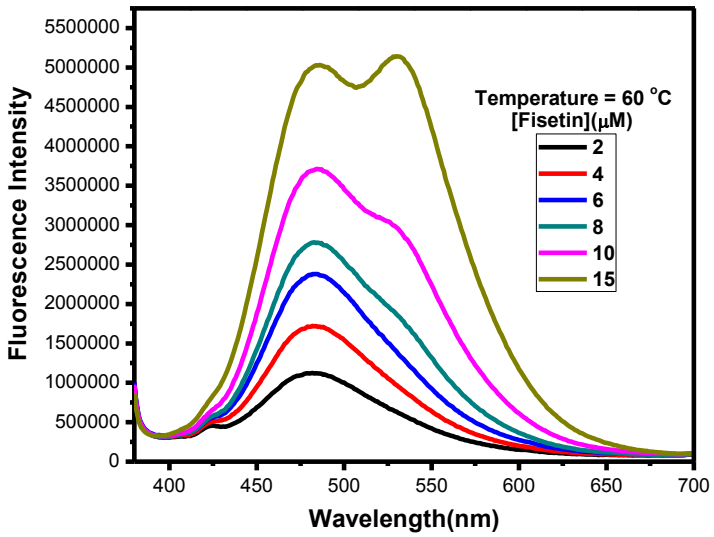

Figure S7. (A) Plot for the variation of tautomeric and anionic emission of fisetin in niosome membrane as a function of temperature. The tautomeric intensity decreases whereas anionic

intensity increases with increase in temperature. (B) Plot for the variation of anionic emission maximum of fisetin in niosome membrane as a function of temperature. There is a red shift in the anionic emission with increase in temperature. [Fisetin] = 5 μM, λ_{ex} = 370 nm.

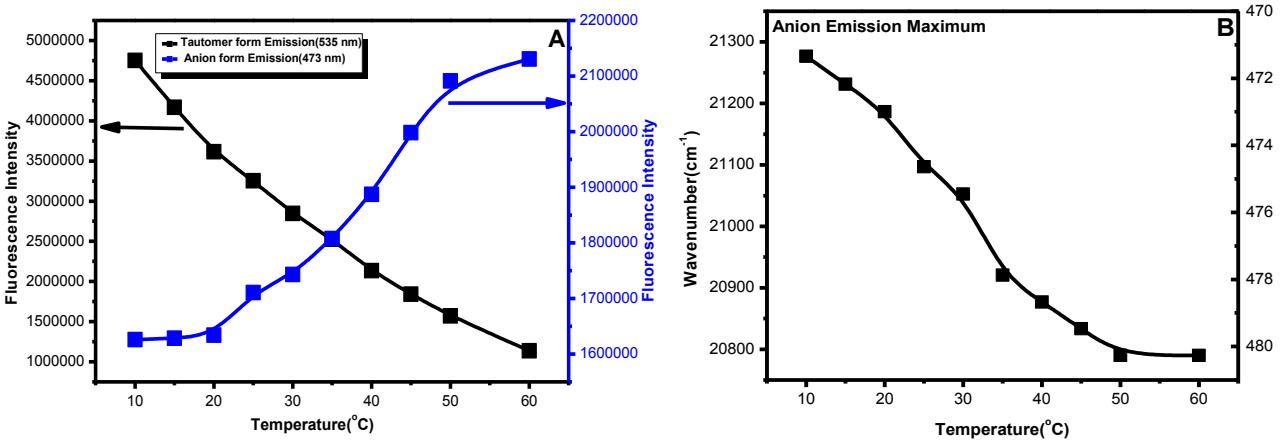

Figure S8: Zeta potential plot of niosome membrane with and without fisetin. The constant value of zeta potential indicates that there is no change in surface charge of niosome membrane in presence of fisetin.

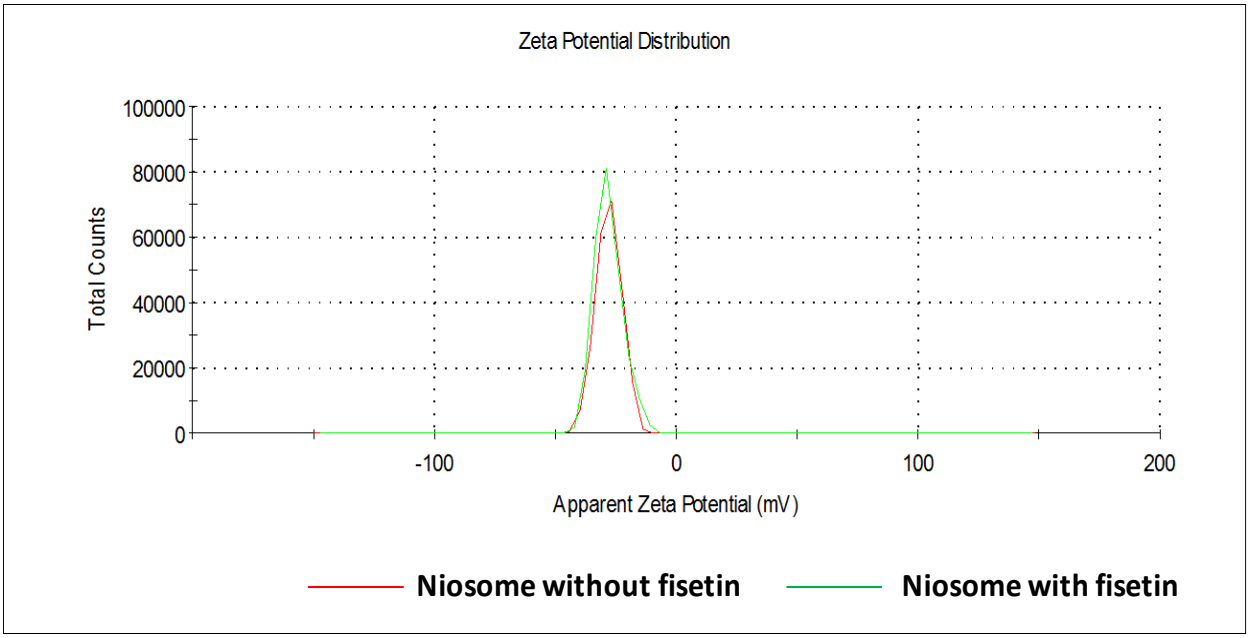

Figure S9. Emission spectra of fisetin (λ_{ex} = 370 nm) in Tween20:cholesterol(1:1) niosomes with varying concentration of CPC at 50 ^{o}C. [Fisetin] = 5 μM, slit width = 5 nm.

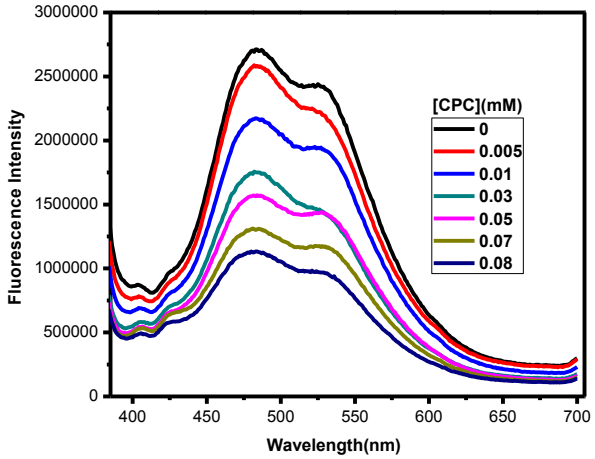

Figure S10. The fluorescence lifetime decay of tautomeric emission of fisetin in TW20:cholesterol(1:1) niosomes with variation of temperature. λ_{ex} = 370 *nm*, λ_{em} = 535 *nm*, [Fisetin] = 5 μM

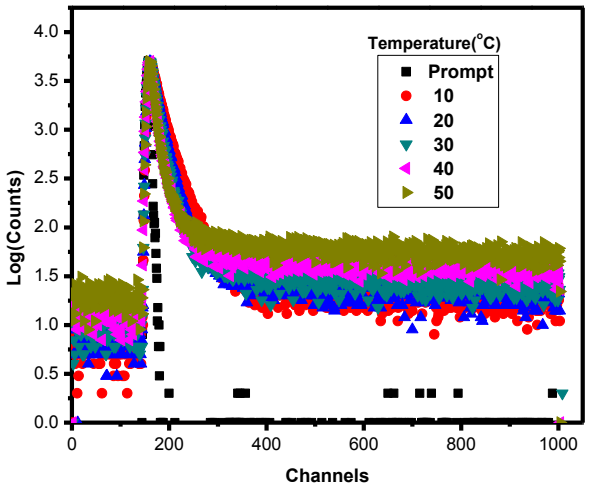

Figure S11. (A) Absorption spectra of DPPH in niosome membrane in presence of fisetin with variation in time.[fisetin] = 5 μM, [DPPH] = 50 μM. With increase in time the absorbance value of radical DPPH(DPPH$^{\cdot}$) decreases along with an increase the absorbance of DPPH-H neutral form. (B) Absorption spectra of DPPH in niosome membrane in presence of fisetin under higher resolution.

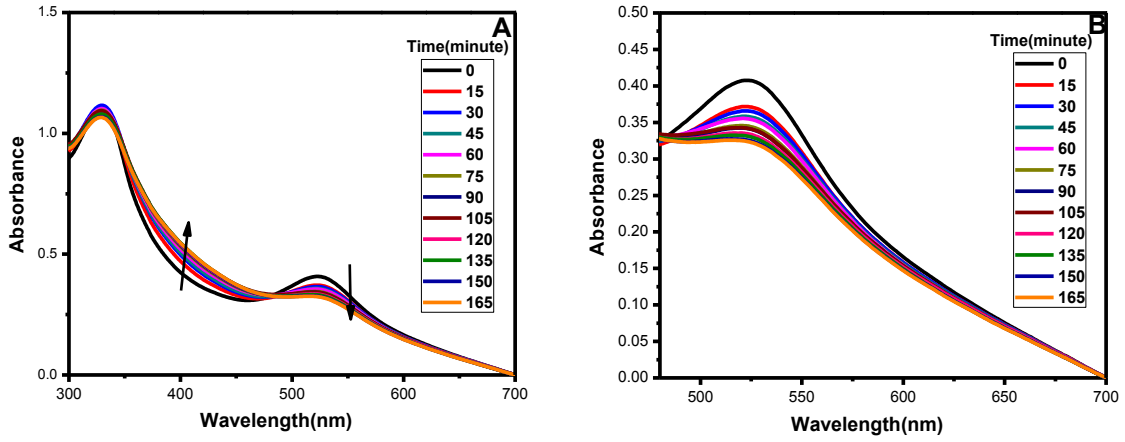

Figure S12. Point plot for the absorbance of $DPPH^{\cdot}$ in niosome membrane in presence of fisetin with variation in time. The decreasing value of absorbance with increase in time indicates the scavenging activity of fisetin.