

Supplementary Information to

Glucose induced self-assembly and phase separation in hydrophilic triblock copolymer solution and its governing mechanism

Divya Patel^a, Amit K. Bhojani^b, Debes Ray^c, Dheeraj K. Singh^b, Debabrata Seth^d, Vinod K. Aswal^c, Ketan Kuperkar^{a*}, Pratap Bahadur^e

^a *Department of Chemistry, Sardar Vallabhbhai National Institute of Technology (SVNIT),
Ichchhanath, Surat-395 007, Gujarat, INDIA.*

^b *Department of Basic Sciences, Institute of Infrastructure Technology Research and Management (IITRAM),
Ahmedabad-380 026, INDIA.*

^c *Solid State Physics Division, Bhabha Atomic Research Centre (BARC),
Trombay, Mumbai, 400 085, Maharashtra, INDIA.*

^d *Department of Chemistry, Indian Institute of Technology (IIT),
Bihta, Patna, 801106, Bihar, INDIA.*

^e *Department of Chemistry, Veer Narmad South Gujarat University (VNSGU),
Udhana-Magdalla road, Surat-395 007, Gujarat, INDIA.*

***Corresponding author:** E-mail: ketankuperkar@gmail.com

Declaration of interest: None

Characterization methods

Small-angle neutron scattering analysis

The differential scattering cross-section per unit volume ($d\Sigma/d\Omega$) as measured for a system of monodisperse particles in a medium can be expressed as

$$\left(\frac{d\Sigma}{d\Omega}\right)(Q) = nV^2 (\rho_p - \rho_s)^2 P(Q)S(Q) + B \quad (1)$$

where n denotes the number density of particles, ρ_p and ρ_s are, respectively, the scattering length densities of particle and solvent and V is the volume of the particle. $P(Q)$ is the intraparticle structure factor and $S(Q)$ is the interparticle structure factor. B is a constant term representing incoherent background, which is mainly due to the hydrogen present in the sample.³⁵⁻³⁶

Intraparticle structure factor $P(Q)$ is decided by the shape and size of the particle and is the square of single-particle form factor $F(Q)$ as determined by

$$P(Q) = \langle |F(Q)|^2 \rangle. \quad (2)$$

For a spherical particle of radius R , $F(Q)$ is given by³⁵

$$F(Q) = 3 \left[\frac{\sin(QR) - QR \cos(QR)}{(QR)^3} \right] \quad (3)$$

The form factor of Gaussian chain coils with the radius of gyration R_g is given by³⁷

$$P(Q) = 2 \frac{\exp(-Q^2 R_g^2) + Q^2 R_g^2 - 1}{(Q^2 R_g^2)^2} \quad (4)$$

The form factor of Gaussian chains is usually used to model the polymer molecules.

Release Kinetics

The release mechanism of curcumin from 5 %w/v F108 with [glucose], M was investigated by four well known mathematical models:^{27, 34,43-45}

Zero-order model

The zero-order model describes systems whose release rates are independent the concentration of the soluble drug. This mathematical model is represented by the following equation:^{34,43}

$$Q_t = K_0 t \quad (5)$$

In this equation, Q_t is the cumulative amount of drug released at time t , and K_0 is the rate constant of zero-order and t is time.

First-order model

The first-order model describes systems whose release rates are dependent on the concentration of the drug. This mathematical model is represented by the following equation:³⁴

$$\log C_t = -\frac{K_1 t}{2.303} \quad (6)$$

In this equation, C_t is the cumulative amount of drug remaining at time t , and K_1 is the rate constant of first-order and t is time.

Higuchi model

According to the Higuchi model, drug release from the system is dependent on the square root of time. In this case, the mechanism of drug release is based on Fick's law. The simplified Higuchi model is represented by the following equation:⁴⁶

$$Q_t = K_H t^{1/2} \quad (7)$$

In this equation, Q_t is the cumulative amount of drug released at time t , and K_H is the rate constant of zero-order and t is time.

Korsmeyer-Peppas model

The Korsmeyer-Peppas model is used to better investigation of the release mechanism. This simple comprehensive model is known as the power law model that describes the release of drugs from polymer systems. In particular, the Korsmeyer-Peppas model can be useful for describing systems whose release mechanism is unclear or several mechanisms are involved. This mathematical model is represented by the following equation:³⁴

$$Q_t = K_{kp} t^n \quad (8)$$

In this equation, Q_t is the cumulative amount of drug released at time t , and K_{KP} is the rate constant of Korsmeyer-Peppas and n is the release exponent.^{34,43}

Results and Discussion

Solution flow behavior

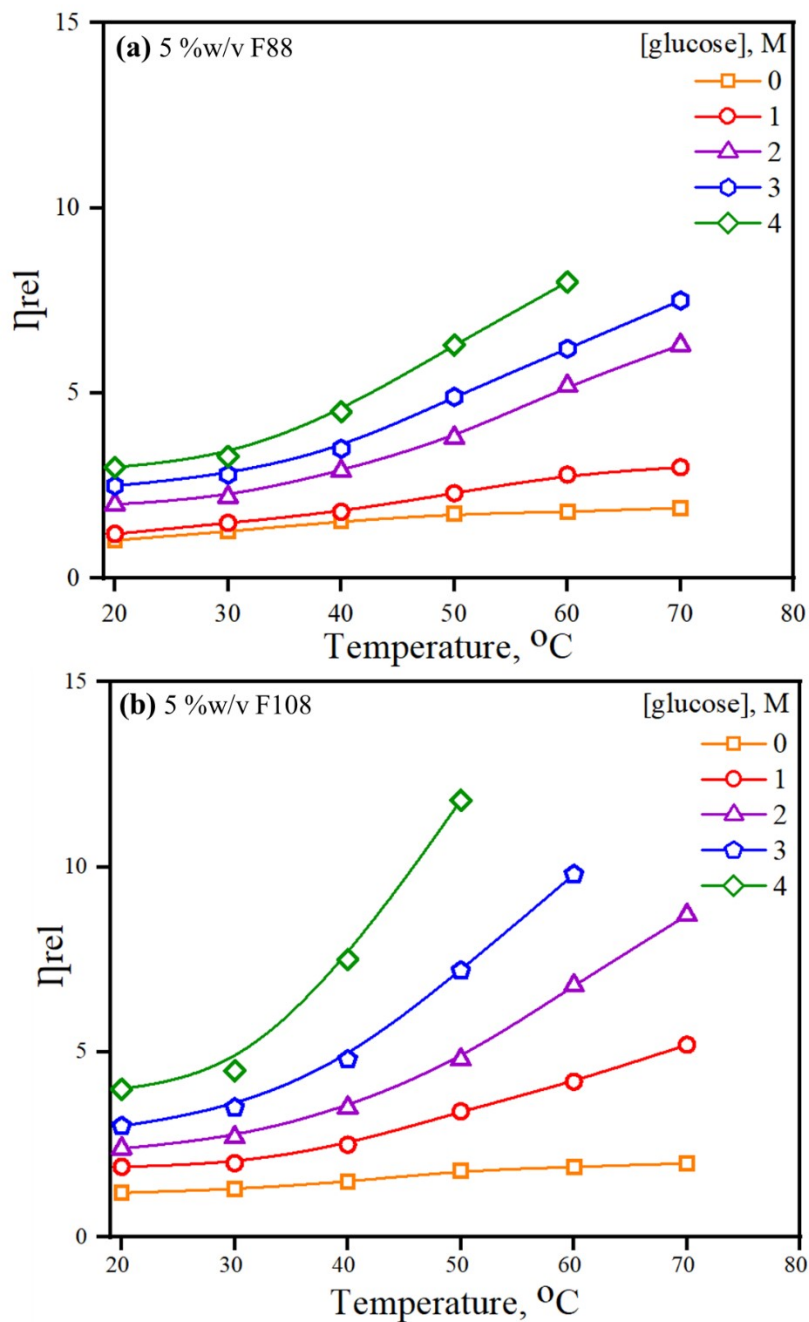


Figure S1: Relative viscosity (η_{rel}) of (a) 5 %w/v F88 and (b) 5 %w/v F108 with varying concentration of glucose.

Micellization conduct

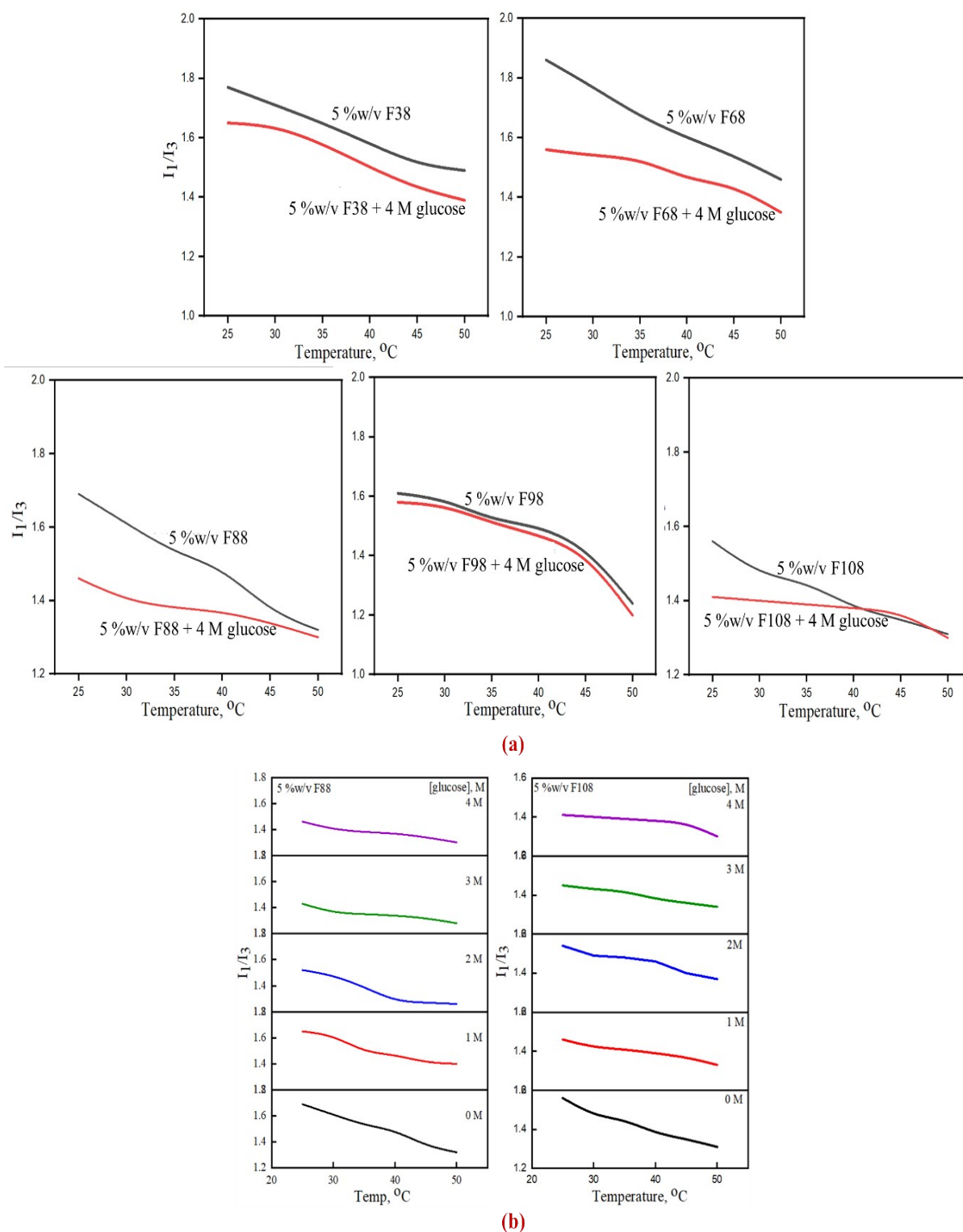


Figure S2: Pyrene fluorescence emission I_1/I_3 intensity ratio plotted against (a) Pluronics® in aqueous and with 4 M glucose and (b) 5 %w/v F88 and 5 %w/v F108 with varying concentration of glucose.

Scattering outline

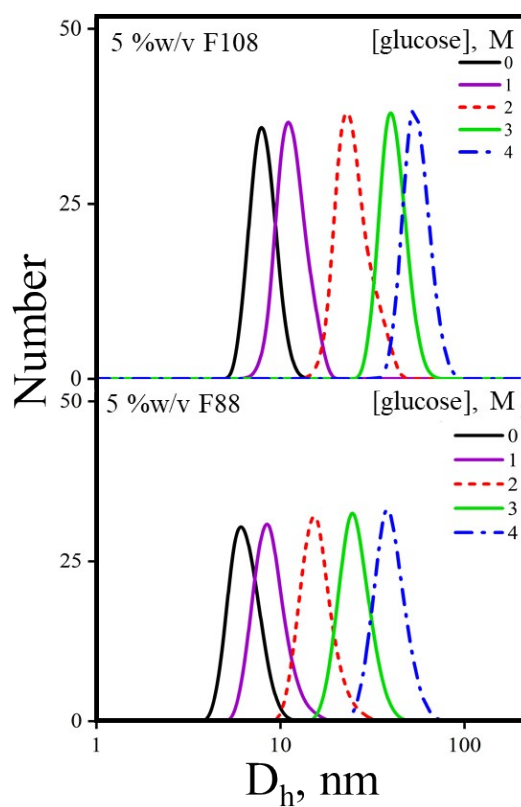


Figure S3: D_h profile for 5 %w/v F88 and 5 %w/v F108 with varying concentration of glucose at 30 °C.

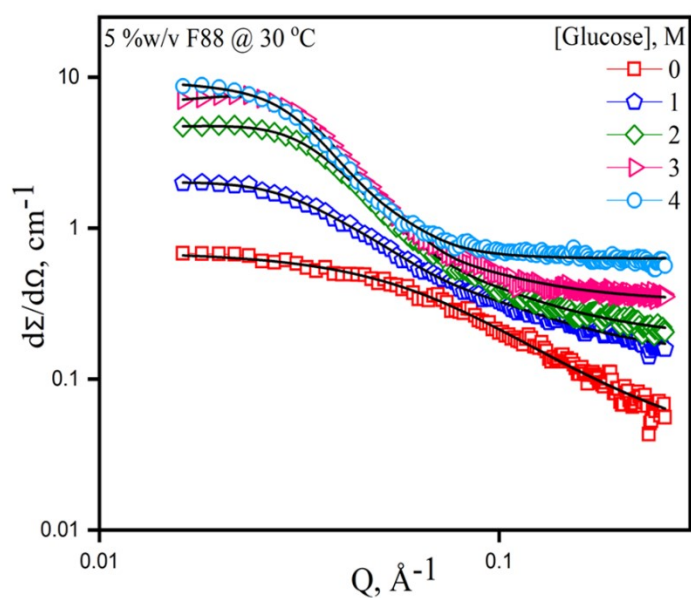


Figure S4: Scattering outline for 5 %w/v F88 with varying concentration of glucose at 30 °C.

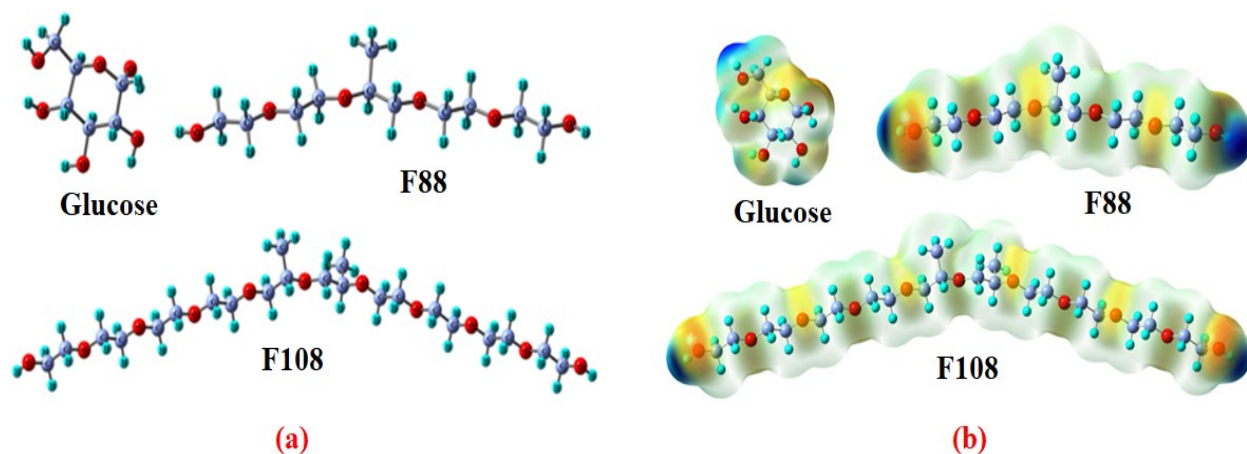


Figure S5: (a) Ground state geometries of glucose, hydrophilic Pluronics[®] (F88 and F108), and glucose with F88 and F108 structures, and (b) Electrostatic potential (ESP) mapped electron density surfaces: glucose, F88, and F108. The red-coloured region represents the negative ESP, whereas, the blue colour indicates the positive ESP region. While zero potential is shown by the green colour on the molecular surface.

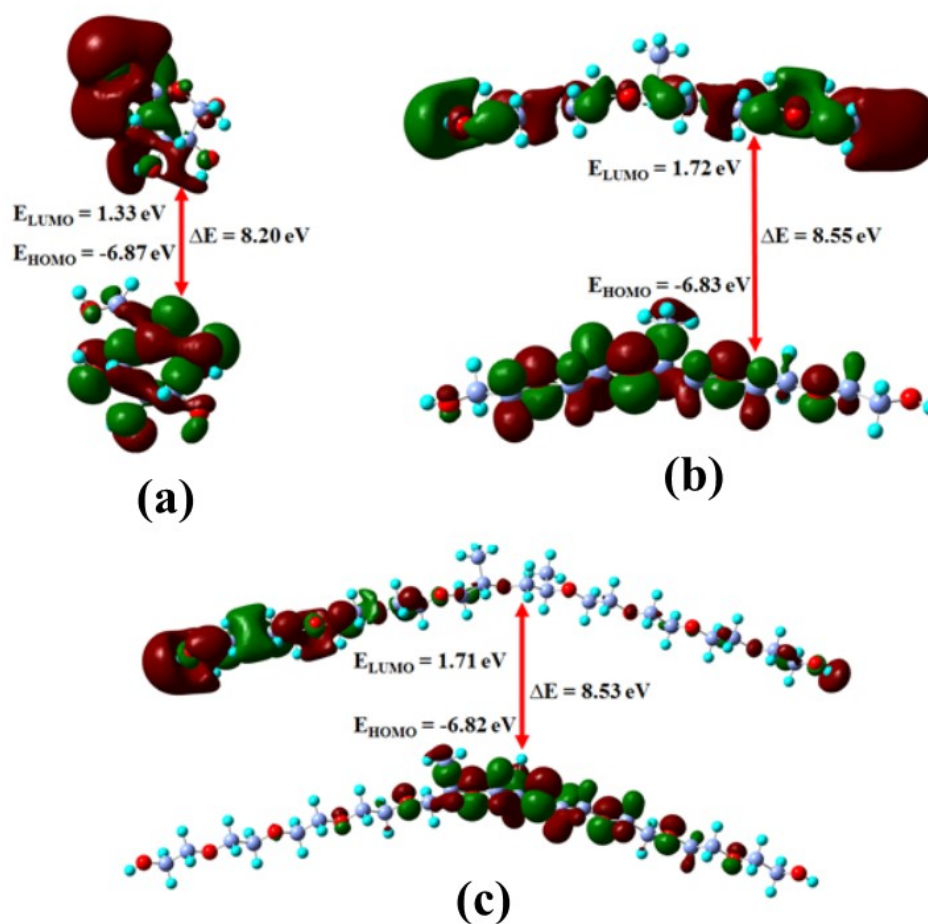


Figure S6: HOMO-LUMO electronic transition along with the energy gap: (a) glucose, (b) F88, and (c) F108 Pluronic[®].

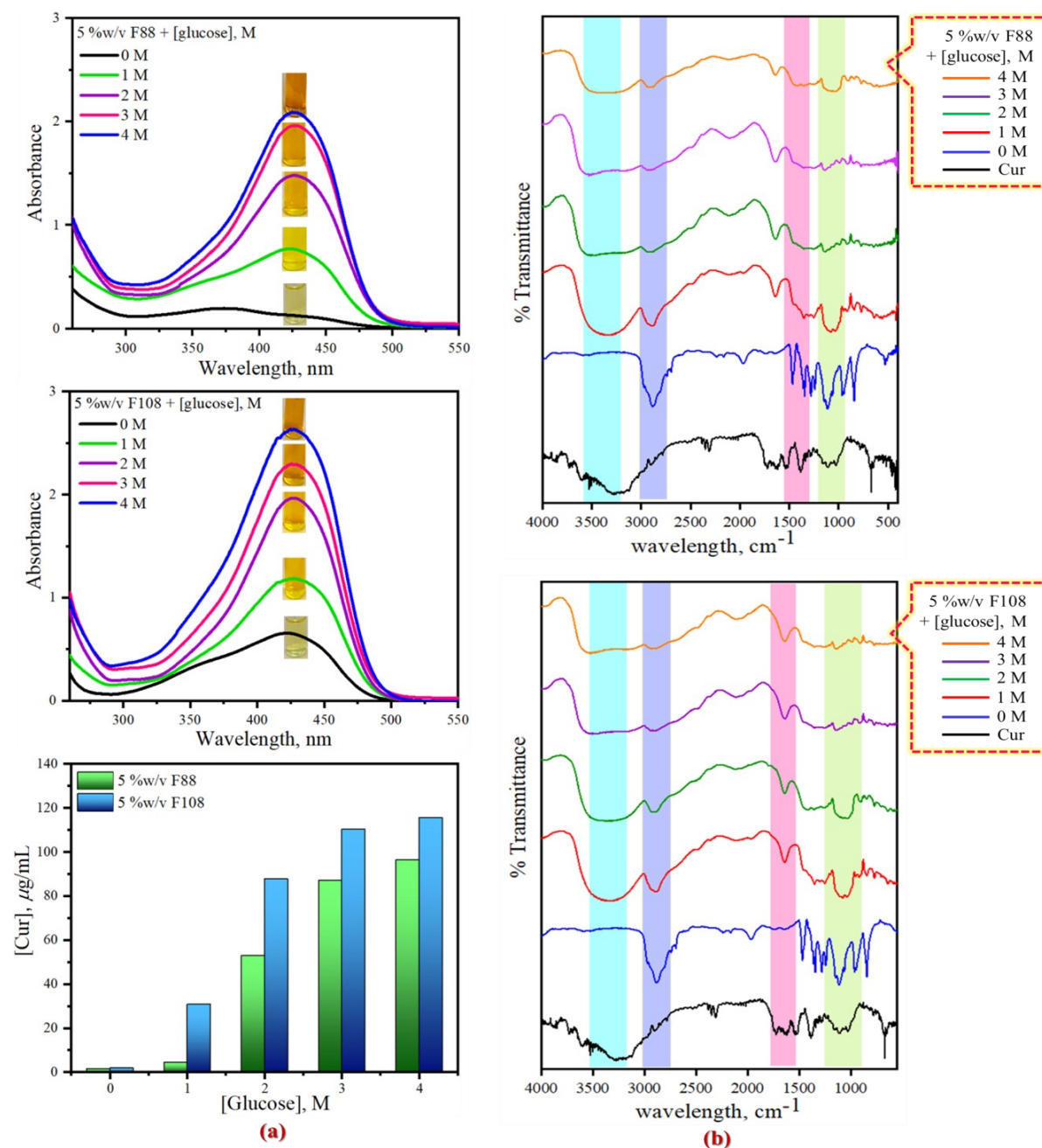


Figure S7: (a) The qualitative analysis of Cur solubilized for 5 %w/v F88, 5 %w/v F108 with increasing concentration of glucose and quantitative analysis of dissolved Cur in the examined systems. (*Insight image is the calibration curve for Cur in ethanol: water ratio*). (b) Spectral (FT-IR) analyses illustrating the influence of Curcumin (Drug) on 5 %w/v F88 and 5 %w/v F108 with different concentration of glucose.