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Kinetics, thermodynamics and isotherm modelling of cloud point extraction of lycopene

Rajendra D. Yadav & Pradip B. Dhamole*

Department of Chemical Engineering, Visvesvaraya National Institute of Technology, Nagpur, Maharashtra-440 010, India

*E-mail: pdhamole@che.vnit.ac.in

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Present work investigates kinetics, thermodynamics and solubilization isotherm of cloud point extraction of lycopene (CPEL) using non-ionic surfactant L62. The kinetics of CPEL has been found to follow pseudo second order with a regression coefficient of 0.99. The experimental data have been fitted to Langmuir adsorption isotherm (R^2 = 0.97) and Freundlich adsorption isotherm (R^2 = 0.96). Surfactant concentration required to extract a given amount of lycopene predicted using Langmuir isotherm is comparable with experimental results (R^2 = 0.96). Thermodynamic parameters obtained for CPEL are: $\Delta H°$= 86.22 kJ/mol and $\Delta S°$ = 0.290 kJ/mol K. $\Delta G°$ is negative for the investigated temperature range (65-85 °C). Lycopene stability data in coacervate phase suggests that the rate of lycopene degradation is best described by a second order kinetic model. Thus, the storage medium found to have influence on lycopene degradation/isomerisation in the surfactant phase.

Keywords: Cloud point extraction, Isotherm, Kinetics, Lycopene, Surfactant, Thermodynamics

Introduction

Lycopene is a naturally occurring compound that belongs to the carotenoid family, which is responsible for the vibrant red and pink colour found in various fruits and vegetables. It is a powerful antioxidant, known for its potential health benefits and its role as a pigment in certain plants[1,2]. Tomato, is a rich source of lycopene. India produces tomato in large quantity (21 million metric tons). For 3 to 4 months during the entire year, there is surplus production of tomato in India[3]. Due to limited storage facility and processing facility, excess production leads to drastic reduction in price of tomatoes resulting to loss to farmers. Existing tomato processing methods require good capital investment[4]. Thus, there is a need of a simple and economical method/process that can be used by farmers to produce valuable/high value products. Recently our group have reported an economical method which uses surfactant for lycopene extraction from whole tomato. This method can also be used for lycopene extraction from tomato processing waste such as tomato peels [6].

Recent research on the micro-emulsion technique and cloud point extraction (CPE) is regarded as a superior option for lycopene extraction, particularly when employing a biocompatible and non-hazardous surfactant[7,8]. This method eliminates the need for back extraction, enhancing its efficiency and safety. Utilizing surfactants for lycopene extraction from tomatoes or any other source facilitates the solubilisation of lycopene in water. CPE is the strong function of surfactant concentration and temperature. The temperature has a significant impact on the phase behaviour of an aqueous non-ionic surfactant solution. Single-phase non-ionic surfactant aqueous solution splits into two phases, a coacervate (lycopene surfactant rich) phase and dilute (rich in water) phase, when incubated above a particular temperature. Cloud point refers to the temperature at which phase separation occurs and cloud point system refers to the phase separation system. However, CPE has several benefits over micro-emulsion as it doesn't require any third component e.g. co-surfactant and organic solvent as in the micro-emulsion technique[9]. Thus, the purity of the product is maintained. Since lycopene is temperature sensitive, one can select a surfactant which has low cloud point temperature as cloud point is based on type of surfactant used. Also if the used surfactant is biocompatible and safe for human consumption, back-extraction is not needed and lycopene can be stored in surfactant form and use as it is. Under this condition, it becomes important to study the stability of lycopene in the coacervate phase.

CPE is a two-way (adsorption-desorption) process involving surfactant micelles and the solute. The solute, lycopene, can be conceptualized as being adsorbed on the surface of a surfactant or at any other micelle junction [11,12]. Therefore, adsorption isotherms can be used for the prediction of the surfactant requirement to get the desired extraction efficiency[13,14]. Further, the rate of lycopene transfer to the coacervate phase can be determined from the kinetic study and thermodynamics of the process. Thus, the current investigation focuses on evaluating the rate of lycopene transfer in the coacervate phase and assessing lycopene stability under different conditions, including variations in temperature, surfactant concentration, and duration. This study aims to deepen our understanding of the factors influencing lycopene behaviour within the coacervate phase. The study is carried out using non-ionic surfactant L62 for lycopene extraction as it is used in skin care products and safe for external application [15].

Further, lycopene stability is a crucial factor in assessing its quality, given its vulnerability to oxidation and isomerization triggered by sensitivity to light and heat. These factors can impact the concentration and overall quality of lycopene. Conversion of the all-trans isomer to the cis-isomer is prone to occur under elevated temperatures or prolonged exposure to light[16]. Hence, kinetics of lycopene degradation was also studied for lycopene concentrated phase (i.e. coacervate phase).

Experimental Section

Materials

The organic solvents used in the current work were of analytical grade and was purchased from Hi-media. Triblock copolymer L62 (polyethylene oxide-polypropylene oxide-polyetheylene oxide i.e.PEO-PPO-PEO) was provided by BASF as a gift sample. L62 has HLB of 7, molar mass 2500 g/mol, and critical micellar concentration 0.0004 M. It was used in its natural state, with no purification. A nearby supermarket supplied the tomatoes for the experiments (Nagpur, Maharashtra). Throughout the experiments, double-distilled water was used.

Lycopene extraction

Tomatoes were ground in a domestic kitchen blender (Sujata Dynamix 900W, 22000 rpm). The obtained puree is further diluted by adding an equal amount of aqueous solution consisting 3% (v/v) L62. The prepared solution was incubated at 30 □ in an incubator shaker (REMI orbital shaking incubator) for 2 h. The solid residue was separated from solution using filtration and the filtrate was used for further studies. Further the filtrate was incubated in a circulating water bath (Polyscience Digital Temperature Controller, USA, MX07R-20-A-12E) at cloud point temperature. This results into two phase formation, dilute phase (DP) and coacervate phase (CP). Lycopene and surfactants are concentrated in the CP, while water along with small quantity of surfactant is present in the DP. The mechanism of lycopene transfers in the coacervate phase during cloud point extraction of lycopene (CPEL) was examined in relation to different parameters. i.e. surfactant concentration, lycopene concentration, temperature and time. Effect of surfactant concentration on CPEL was studied by adjusting the surfactant concentration in the filtrate at the desired level (3-15% v/v). This was done based on the initial surfactant present in the filtrate. Similarly, the effect of lycopene concentration on CPEL was studied by diluting the filtrate with distilled water and bringing the lycopene level to the desired concentration (1-5% w/v). Effect of temperature (65-85 °C) and phase separation time (0-30 min) on lycopene extraction efficiency was studied for 3% (v/v) L62.

Further the stability of lycopene in the CP was also investigated. The motive for conducting stability test for lycopene in the CP was to obtain an optimal storage condition that has low impact on lycopene quality and rate of deterioration. All the CPE and stability studies were carried out in graduated test tubes (15 mL) having sample volume of 10 mL. Amount of lycopene in CP and DP was determined using a method reported earlier (Fish *et al*., 2002). After phase separation, the volume and lycopene content of both the phases were determined. Time required for phase separation was also monitored. All the experiments were carried out in duplicate. Further the obtained results were expressed in terms of extraction efficiency, partition coefficient and are estimated using Eqs. (1) and (2), respectively [14].

$$Extraction\ efficiency\ (\%) = \left(1 - \frac{C_{lcd} * V_{vd}}{C_{lco} * V_{vo}}\right) \quad \ldots (1)$$

$$Partition\ coefficient\ (K_l) = \frac{C_{lcc}}{C_{lcd}} \quad \ldots (2)$$

Where, C_{lco} represents initial lycopene concentration in a sample of known volume V_{vo}.

The lycopene concentration in the DP and CP is represented by C_{lcd} and C_{lcc}, respecively. V_{vd} and V_{vc} is the volume of dilute and coacervate phase, respectively.

Lycopene analysis

Lycopene content in DP and CP was analysed using the method reported earlier by Fish *et al.*[17.] The specifics of the process are reported elsewhere [18,19], and estimated using Eqs (3) and (4). The absorbance was measured using a UV-visible spectrophotometer (Agilent Technologies Cary 60 UV-VIS). Extraction efficiency of lycopene was determined by measuring the lycopene content of the sample, before and after the extraction and calculated using Eq. (5). Results were confirmed using material balance of lycopene.

$$Lycopene\left(\frac{mg}{kg}tissue\right) = \frac{A_{503}*536.9g*1L*10^3\,mg*10mL}{17.2*\frac{10^4}{M}*cm*10^3ml*1g*kg\ tissue} \quad \ldots (3)$$

$$Lycopene\left(\frac{mg}{kg}tissue\right) = \frac{A_{503}*31.2}{g\ tissue} \quad \ldots (4)$$

$$\%Lycopene\ extraction = \frac{Lycopene\ extracted\ (\frac{mg}{kg})}{Initial\ lycopene\ present\ in\ pomace(\frac{mg}{kg})}x100 \quad \ldots (5)$$

Where A_{503} is absorbance at wavelength of 503 nm, 536.9 g/mol is the molecular weight, $17.2*10^4$ is molar extinction coefficient.

Stability of lycopene in coacervate phase

The effect of different parameters i.e. temperature, surfactant concentration, and time, was taken into consideration for the determination of lycopene stability in coacervate phase. After CPEL coacervate phase (10 mL) was distributed into 15 mL sample vials. For 7 days, the vials were incubated at various temperatures between 30 and 50 °C. Every 24 h, a sample of 1 mL was taken and passed through a spectrophotometer for analysis. Effect of surfactant concentration (20 to 40% v/v) on stability of lycopene was investigated. The sample vials were then incubated at 40 °C for 7 days. The samples were collected and examined after 7 days. However for storage of greater time period the antioxidants can be used. The different type of antioxidants such as lipophilic tert-butylhydroquinone (TBHQ) and amphiphilic (lauryl gallate) could be added to avoid lycopene degradation/isomerisation[5].

Kinetics of lycopene degradation in coacervate phase

The experimental data for the determination of degradation rate of lycopene in surfactant phase in two variables, C_{a0} and C_a. C_{a0} represents initial lycopene concentration in surfactant phase and C_a is the lycopene concentration in surfactant phase at any time t. The kinetics of lycopene degradation for zero, 1st and 2nd order is represented by the Eqs. (6), (7) and (8) [20,21].

$$C_{a0} - C_a = k_1 * t \quad \ldots (6)$$

$$\ln\left(\frac{C_{0a}}{C_a}\right) = k_2 * t \quad \ldots (7)$$

$$\frac{1}{C_a} = \frac{1}{C_{a0}} + k_3 * t \quad \ldots (8)$$

Where k_1, k_2 and k_3 are the reaction rate constant for zero, 1st and 2nd order, which was determined using linear plots of above equation (LHS of above equations vs. t). The kinetic equation that fits the experimental data more accurate was determined using correlation coefficients.

Arrhenius Eqs. (9) and (10) were used to calculate the impact of temperature on the reaction rate constant and activation energy.

$$k = k_0 * e^{-(\frac{E}{RT})} \quad \ldots (9)$$

$$\ln(k) = \ln(k_0) - \frac{E}{RT} \quad \ldots (10)$$

Here k is the reaction rate constant at fixed temperature T (K), E is the activation energy (kJ/mol), R is the universal gas constant (8.314 J/(mol K)) and k_0 is the pre-exponential factor (h^{-1}). E is estimated using linear plot of ln(k) vs. 1/T at different temperature ranging from (30-50 °C).

Activation enthalpy (ΔH) as per activated complex theory was determined using following equation [22].

$$\ln\left(\frac{k}{T}\right) = -\frac{\Delta H}{RT} + \frac{S}{R} + \ln\left(\frac{kb}{h}\right) \quad \ldots (11)$$

Where k_b is Boltzmann constant and h is Planck's constant. Using linear plots of ln (k/T) vs. (1/T) at different temperature, ΔH is computed.

The spontaneity of the process was examined using the Gibbs free energy equation.

$$\Delta G = -R * T \ln(k) \quad \ldots (12)$$

Results and Discussion

Parameter impacting CPEL

Different factors that affect CPEL were investigated to gather the necessary experimental data

for conducting studies on kinetics, thermodynamics, and isotherms. Parameters include surfactant concentration, lycopene concentration, temperature and time. It was observed that the CPEL increased from 447 (78%) to 551 (98%) mg/kg, respectively [40], with increase in surfactant concentration from 3-15% (v/v). However, as the concentration of L62 increased the partition coefficient decreased from 20.99 to 12.87 [5]. Increased surfactant concentration would lead to more micelle formation and thus enhanced solubilisation of lycopene [23]. Decrease in partition coefficient, was due to increased solubilisation of lycopene in the CP and the increase in CP volume, thus decreasing the concentration of lycopene in the CP.

Effect of lycopene concentration (1% to 5% w/v) was studied on CPEL at 65 °C for 3% L62 (30 min). The CPEL decreased from 556 (98.9%) to 441 (78.5%) mg/kg with an increase in lycopene concentration (Fig. 1a). Partition coefficient of lycopene decreased from 514 to 32.9 with increase in lycopene concentration (Fig. 1a). The decrease in extraction efficiency was due to constant surfactant concentration, which fixes the solubilisation capacity of the lycopene. Since the lycopene concentration increases and the solubilisation capacity remains constant, the insolubilized lycopene will remain in the dilute phase. This would result in lowering extraction efficiency and decreased partition coefficient of lycopene.

Since lycopene is sensitive to temperature, it is necessary to investigate how temperature affects lycopene recovery [24,25]. CPEL increases from 460 (82.4%) to 543 (96.1%) mg/kg, with rise in temperature from 65 °C to 85 °C (data not shown in the presesnt article). A higher temperature would reduce the exposure time of lycopene and improve the phase separation process. Increase in temperature results in dehydration of surfactant that would increase the micelles. Moreover, the CMC of a surfactant decreases as temperature increases [25]. Therefore a rise in temperature results in an overall improvement in extraction efficiency.

Effect of incubation time (0-30 min) was studied on CPE of lycopene at 65 °C for 3% L62. It was observed that two phase separation required 10 min. Incubation beyond 10 minutes had insignificant effect on extraction efficiency (444 (79%)-465 (82.8%) mg/kg) and fractional CP volume (0.09 to 0.11) (Fig. 2). Thus, the equilibrium is reached in 10 min. Fig. 2 shows different time zones of phase separation. Zone 1 represents the region of a single phase. Zone 2 represents the region of phase transition from single to two phases and zone 3 represents a complete two-phase formation. Thus, it can be considered that the phase transition takes place in between 5 to 10 min.

Kinetics of CPEL

In the present work, for the determination of kinetics of CPEL three different models were fitted to the experimental data, i.e. intra-particle diffusion model, pseudo first order (PFO) and second order models (PSO) [26]. The experimental data of lycopene solubilized in CP at 65 °C was used to fit the above

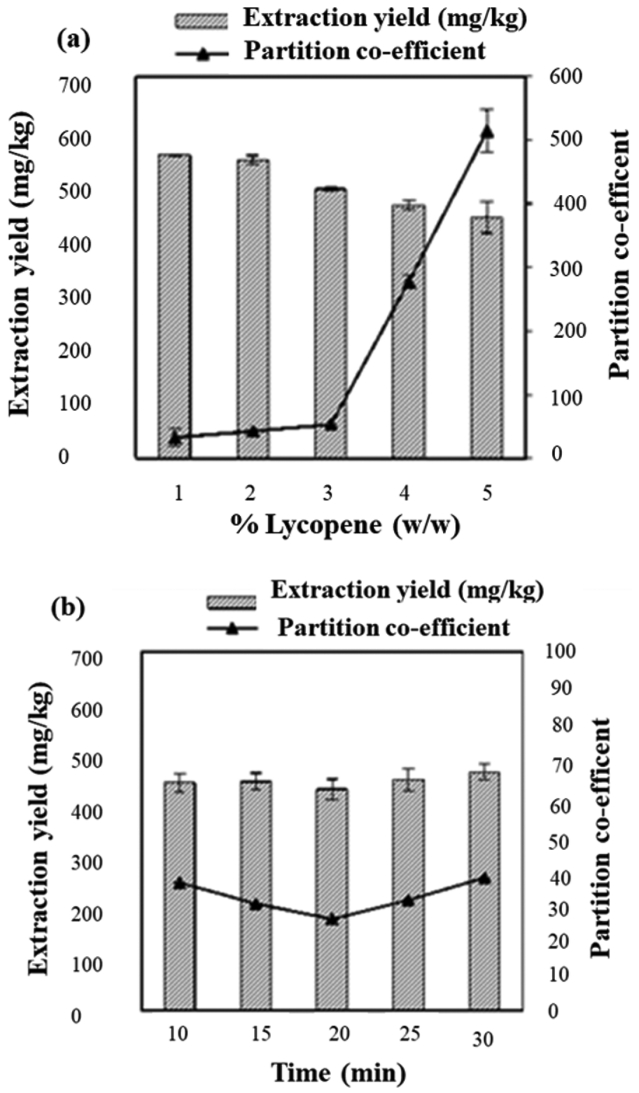

Fig. 1 — (a) Effect of lycopene concentration CPEL and lycopene partition coefficient (T = 65 °C, time = 30 min, L62 = 3% (v/v)) and (b) impact of phase separation time on extraction (T = 65 °C, initial lycopene concentration = 5.62 g /L, L62 = 3% (v/v))

models (Fig. 3). The PFO equation of Lagergren in linearized form is given by Eq. (13) [27,28].

$$ln\,(q_e - q) = ln\,(q_e) - K_1 * t \quad \ldots (13)$$

Where q_e is the lycopene adsorbed in the CP at equilibrium and q is the lycopene adsorbed in the coacervate at any time t, K_1 is the rate constant of PFO adsorption (min^{-1}) (Fig. 3a).

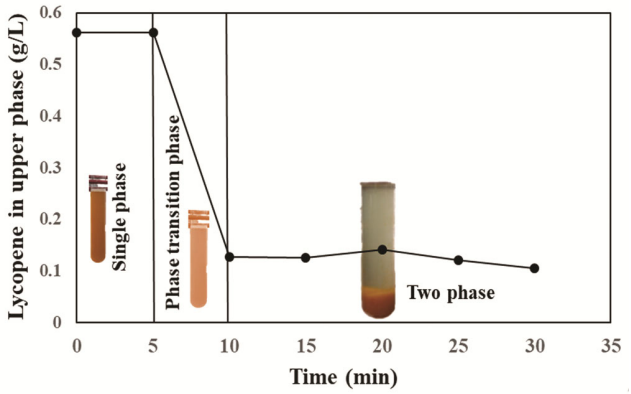

Fig. 2 — Systematic representation of phase transition zones (T = 65 °C, initial lycopene concentration = 5.62 g /L, L62 = 3% (v/v))

The linearized form of the PSO equation is given by the Eq. (14). The plot of t/q vs. t gives the rate constant K_2 value (Fig. 3b) [29].

$$\frac{t}{q} = \frac{1}{qe^2 * K_2} + \frac{t}{q_e} \quad \ldots (14)$$

Eq. (15) represents an intra-particle diffusion model of lycopene in the coacervate phase.

$$q\_ = t\text{^}0.5 * K\_3 + C \quad \ldots (15)$$

Where C represents the intercept value from the plot and K_3 is the intra-particle diffusion rate constant (mg/g)*$min^{0.5}$), which is the slope obtained from plot Fig. 3c.

The regression coefficient value and rate constants for all the models were estimated (Table 1). The plots of t/q versus t show a good R^2 value greater than 0.9. Thus, it can be said that lycopene extraction in CP is a second-order kinetic model.

Thermodynamics of CPEL

In order to assess how temperature affects the extraction of lycopene, multiple thermodynamic parameters including changes in Gibbs free energy

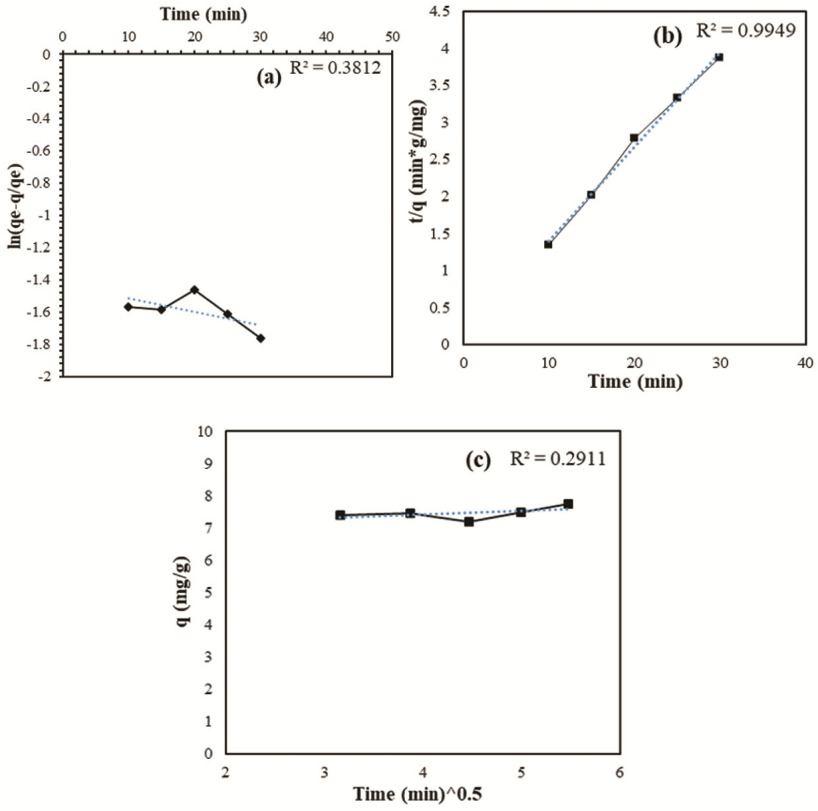

Fig. 3 — (a) PFO kinetics, (b) PSO kinetics and (c) intra-particle diffusion model (Operating conditions: T = 65 °C, initial lycopene concentration = 5.62 g /L, initial fixed L62 concentration = 3% (v/v))

Table 1 — Regression coefficient and rate constant for different models used for determination of kinetics of CPEL

Kinetics model	Rate constant	R^2
PFO	0.008 min^{-1}	0.38
PSO	0.09 mg/g $min^{0.5}$	0.99
Intra-particle diffusion model	0.12	0.29

Table 2 — Thermodynamic parameters for CPEL

Temperature (K)	$\Delta G°$ (kJ/mol)	$\Delta H°$ (kJ/mol)	$\Delta S°$(kJ/mol K)
338	-11.89	86.22	0.290
343	-13.46		
348	-14.79		
353	-16.35		
358	-17.7		

($\Delta G°$), enthalpy ($\Delta H°$), and entropy (ΔS°), were determined (Eqs. (16), (17)) (Table 2) [30].

$$\Delta G° = -R * T * ln(k) \quad \text{... (16)}$$

$$ln(k) = \frac{\Delta S°}{R} - \frac{\Delta H°}{R*T} \quad \text{... (17)}$$

Where, k is the equilibrium constant that is defined as the ratio of solublization capacity of lycopene in the CP (mg/mg) to the concentration of lycopene in the DP (mg/L) [27,31]. R (8.314 (J/K mol)) and T (K) is the universal gas constant and temperature. The plot of ln(k) vs. 1/T gives the value of $\Delta H°$ and $\Delta S°$ using Eq. (17). The value of $\Delta G°$ ranges from -11.89 to -17.7 (kJ/mol). A -$\Delta G°$ value presents the spontaneity of the process as the temperature increases from 65 to 85 °C, the -$\Delta G°$ also increases. It showed that the process is more spontaneous at high temperatures. The plot of ln(k) versus 1/T gives the value of $\Delta H°$ and $\Delta S°$. The positive valves of $\Delta H°$, i.e., 86.22 (kJ/mol) indicate the process is endothermic and there is a strong interaction between surfactant (adsorbent) and lycopene (adsorbate). The positive value of $\Delta S°$ i.e. 0.290 (kJ/mol K) suggests some structural changes in surfactant micelle [27,31].

Solubilization isotherm of lycopene in surfactant

Isotherm study helps to find the equilibrium relationship between the adsorbate concentration in liquid phase and equilibrium absorption amount on solid phase at a specific temperature. Adsorption model also helps to find adsorption mechanism, maximum adsorption capacity and properties of adsorbent.

In the present article surfactant (L62) was considered as an adsorbent and lycopene as an adsorbate in an aqueous solution. The data were applied to two adsorption isotherms, Freundlich and Langmuir isotherms.

The Langmuir isotherm (Eq. 19) [32-34] was used to describe the partitioning of the solute (lycopene) in the coacervate phase. The adsorption of lycopene by surfactant L62 micelles was assumed to be a homogeneous monolayer.

$$q = \frac{(k*p*C_{lcd})}{(1+C_{lcd})} \quad \text{... (18)}$$

$$\frac{1}{q} = \frac{1}{k} + \frac{1}{(k*p*C_{lcd})} \quad \text{... (19)}$$

Where q denotes the quantity of lycopene molecularly soluble with L62, C_{lcd} is the lycopene concentration in DP; k and p are the Langmuir constants (k - solublization capacity of adsorbent and p -the energy of solublization).

The Freundlich isotherm (Eq. 20) [35] describes the interaction of the bound and free lycopene by a power function.

$$q = a * {C_{lcd}}^m \quad \text{... (20)}$$

$$Log\ (q) = Log(a) + m * Log(C_{lcd}) \quad \text{... (21)}$$

Where, *a* and *m* represent Freundlich constants.

For the determination of Langmuir constants, the graph of 1/q vs $1/_{Clcd}$ was plotted using Eq. (19) (Fig. 4a). It was found that Langmuir constants, k, and p, have values of 0.057 (mol/mol) and 175.2 (L/mmol) for the lycopene-L62 system. For the determination of Freundlich constants, the graph of Log (q) vs. Log (C_{lcd}) was plotted using Eq. (22) (Fig. 4b). It was found that Freundlich constants, a, and m, have values 0.66 (mol/mol) and 0.273 (L/mol) for the lycopene-L62 system. Langmuir adsorption isotherm (R^2 = 0.97) was found to be a better fit for the lycopene-L62 system.

Development of a theoretical equation for the amount of surfactant required for desired lycopene extraction

Theoretical equation helps to predict the amount of surfactant required for obtaining desired lycopene

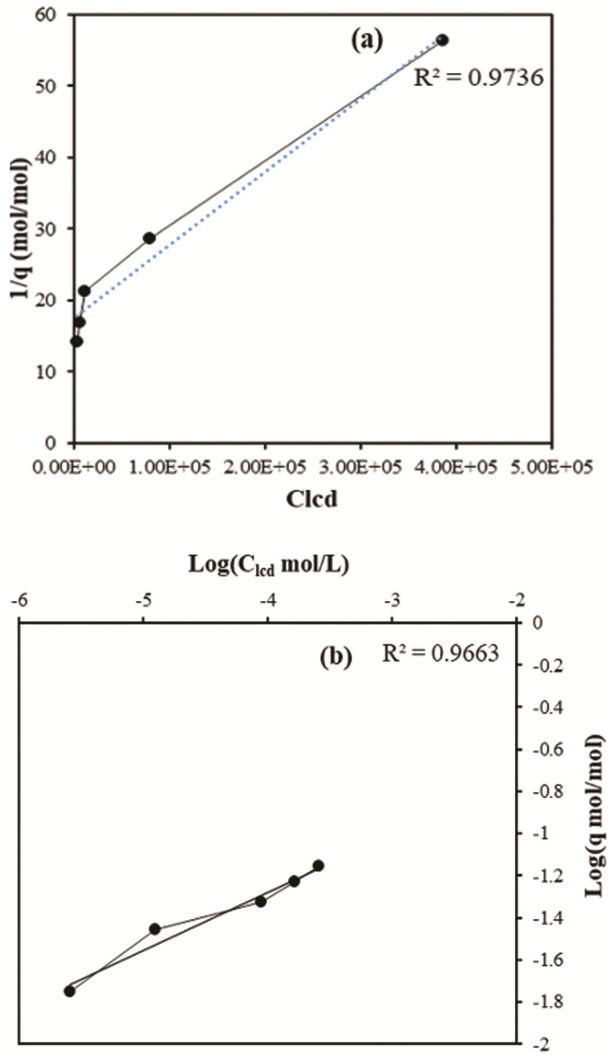

Fig. 4 — (a) Langmuir constant plot for calculating the Langmuir constants *k* and *p* and (b) Freundlich isotherm plot for calculating the Freundlich constants *a* and *m*

extraction in CPEL, which helps in design of CPE extractor for scale up. Basic adsorption equations were used for development of theoretical equation that predicts lycopene extraction efficiency at fixed surfactant concentration. Further to predict the effectiveness of theoretical equation the obtained results were compared with experimental data. The adsorption (q) of lycopene in the CP is defined as:

$$q = \frac{C_{lcc}}{C_{scc}} \quad \text{... (22)}$$

The extraction efficiency of solute (E) from the aqueous phase to the CP during the CPE process is given by Eq. (23).

$$E = \frac{Amount\ of\ lycopene\ in\ coacervate\ phase}{Initial\ amount\ of\ lycopene\ in\ feed}$$

$$E = \frac{C_{lcc}*V_{vc}}{C_{lco}*V_{vo}} \quad \text{... (23)}$$

$$E = \frac{C_{lcc}*(V_{vo}-V_{vd})}{C_{lco}*V_{vo}} \quad \text{... (24)}$$

Where, C_{lcc} = lycopene concentration in the CP, C_{scc} = concentration of surfactant in the CP, C_{lco} = initial lycopene concentration, V_{vo} = initial volume of solution, V_{vd} = DP volume and V_{vc} = CP volume.

The surfactant concentration L62 in the CP (C_{scc}) can be expressed as:

$$C_{scc} = \frac{Amount\ of\ L62\ in\ coacervate\ phase}{volume\ of\ coacervate\ phase} = \frac{C_{sco}*V_{vo}-C_{scd}*V_{vd}}{V_{vo}-V_{vd}} \quad \text{... (25)}$$

Where C_{sco} and C_{scd} are initial surfactants (L62) concentrations in the aqueous system and surfactant (L62) concentrations present in the dilute phase.

Rearranging equations (24) – (25) leads to:

$$\frac{1}{q} = \frac{C_{sco}*V_{vo}-C_{scd}*V_{vd}}{E*C_{lco}*V_{vo}} = \frac{C_{sco}}{E*C_{lco}} - \frac{C_{scd}*V_{vd}}{E*C_{lco}*V_{vo}} \quad \text{... (26)}$$

Since surfactant concentration in CP is significantly higher than DP (close to CMC of surfactant), Eq. (27) can be written as

$$\frac{1}{q} = \frac{C_{sco}}{E*C_{lco}} \quad \text{... (27)}$$

Lycopene concentration in DP (C_{lcd}) can be represented as:

$$C_{lcd} = amount\ of\ lycopene\ in\ dilute\ phase / Volume\ of\ dilute\ phase$$

Using material balance above equation can be written as:

$$C_{lcd} = \frac{C_{lco}*V_{vo}-C_{lcc*}V_{vc}}{V_{vd}} = \frac{C_{lco}*V_{vo}-C_{lcc}*(V_{vo}-V_{vd})}{V_{vd}} \quad \text{... (28)}$$

The result of rearranging Eqs. (18) and (23) is:

$$C_{lcd} = \frac{C_{lco}*V_{vo}-E*C_{lco}*V_{vo}}{V_{vd}} \quad \text{... (29)}$$

The DP volume (V_{vd}) is much higher than the volume (V_{vc}) of the CP. So the total volume can be considered to be equal to the initial volume of the system (V_{vo}).

$$C_{lcd} = C_{lco*}(1-E)$$

From equations (18), (27), (29), C_{sco} can be expressed as

$$C_{sco} = \frac{E}{k*p*(1-E)} + \frac{E*C_{lco}}{k} \quad \text{... (30)}$$

Thus, the amount of surfactant needed to achieve desired extraction efficiency for a known initial lycopene concentration can be predicted using Eq. (30), provided that the Langmuir constants k and p are known. Eq. (30) was validated with experimental results. To determine the extraction efficiency at different surfactant concentrations, experiments were performed. The amount of surfactant required to achieve the same efficiency was estimated using Eq. (30). It can be seen that the surfactant concentration predicted using Eq. (30) matches well with the experimental results (Fig. 5a). For the theoretical extraction efficiency of 85% (w/w), the required concentration of surfactant L62 for varying initial lycopene concentrations ranging from ($2.12x10^{-7}$ to $8.4x10^{-7}$ mol/L) is plotted in Fig. 5b using Eq. (30).

Kinetics and thermodynamics of lycopene degradation

Due to sensitive nature of lycopene, a study on the aforementioned topic is required to determine how temperature and surfactant concentration affect it. The obtained optimized results help to predict proper storage conditions that minimize losses.

Kinetic of lycopene degradation in surfactant phase

The rate constant and correlation coefficient (R^2) for different kinetic model at different temperatures (30-50 °C) are given in Table 3. Correlation coefficient (R^2) values at each temperature for different models were compared and models that have R^2 value close to unity was selected. The lycopene degradation/isomerization in surfactant phase was best expressed by the second order kinetic model [25]. The rate of degradation was rapid initially, then gradually decreased. This may be due to freely available lycopene which was exposed to heat (Fig. 6c). Surfactant protected the lycopene from

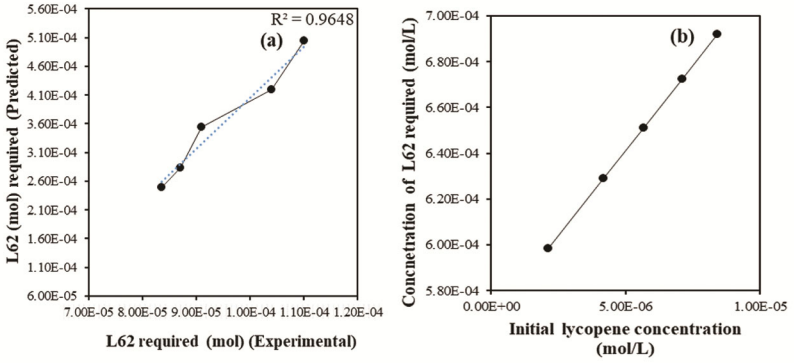

Fig. 5 — Plot of (a) experimental vs. predicted values of L62 and (b) initial lycopene concentration vs.concentration of L62 required

Table 3 — Reaction rate constant (k) and correlation coefficient (R^2) of three kinetic models at different temperature

S No.	Temperature (°C)	Order of reaction	Rate constant value (x 10^{-3})	Correlation co-efficient (R^2)
1.	30	Zero order	72.6 h^{-1} * (mg/L)	0.983
		1st order	1.3 h^{-1}	0.986
		2nd order	0.02 h^{-1} * $(mg/L)^{-1}$	0.988
2.	35	Zero order	92.8 h^{-1} * (mg/L)	0.887
		1ST order	1.7 h^{-1}	0.897
		2nd order	.03 h^{-1} * $(mg/L)^{-1}$	0.906
3.	40	Zero order	179.9 h^{-1} * (mg/L)	0.968
		1ST order	3.9 h^{-1}	0.956
		2nd order	0.09 h^{-1} * $(mg/L)^{-1}$	0.937
4.	45	Zero order	209 h^{-1} * (mg/L)	0.912
		1ST order	0.052 h^{-1}	0.950
		2nd order	0.1 h^{-1} * $(mg/L)^{-1}$	0.974
5.	50	Zero order	206.1 h^{-1} * (mg/L)	0.839
		1ST order	5.9 h^{-1}	0.924
		2nd order	0.2 h^{-1} * $(mg/L)^{-1}$	0.955

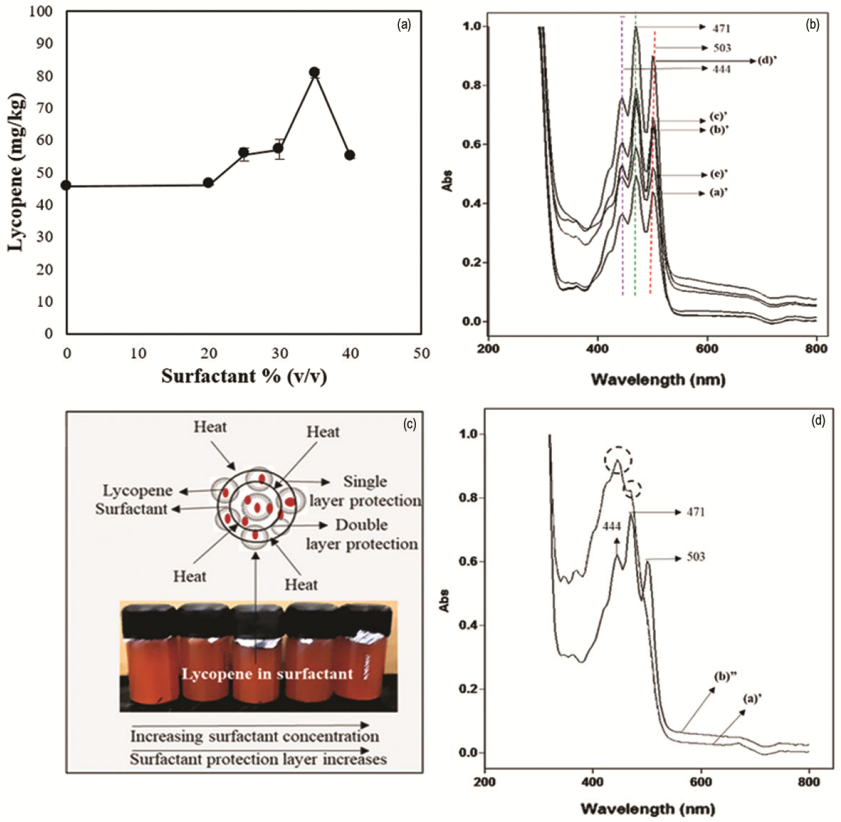

Fig. 6 — (a) Effect of surfactant concentration on lycopene in surfactant phase (Extract (Lycopene surfactant phase) = 1 mL, initial lycopene = 128.4 (mg/kg), Surfactant concentration = (20-40% (v/v)), temperature = 40 °C, incubation time 7 days), (b) UV-visible absorption spectra of samples with different surfactant concentration (a', b', c', d' and e' correspond 20, 25, 30, 35 and 40% (v/v)), (c) systematic representation of protection behaviour of surfactant and (d) effect of temperature on lycopene for temperature greater than 100 °C and time above 162 h

further degradation. Thus surfactant is not responsible for degradation, as shown in Fig. 6a. Since lycopene is sensitive to light and heat, the temperature only affects kinetics from isomerization or degradation. The rate of lycopene degradation in the surfactant L62 model system was found to be less than in water system [25]. This is due to the hydrophobic nature of surfactants, which absorbs lycopene and develops a hypothetical layer. The potential of oxygen to react with lycopene present directly decreases by providing some sort of a ''blocking action'', leading to the decrease in the available oxygen that can get associated with lycopene directly.

The lycopene peak during UV spectrophotometer analysis is observed at three different wavelength 444, 471 and 503 nm. The interference of other carotenoid such as β-carotene is less at 503 nm [17]. Thus from Fig. 6d, in sample a' the absence of peak at 503 nm conclude that lycopene stability is less compared to β-carotene or else the lycopene degradation rate is more when present in pure form at temperature above 100 °C and time interval greater than 168 h.

Thermodynamic of lycopene degradation in surfactant phase

The thermodynamic of lycopene degradation was studied by determining the different factor such as activation energy, activation enthalpy and activation entropy. Activation energy of 94.62 (kJ/mol)) was obtained using slope of logarithmic plot ln(k) vs. 1/T (Fig. 7a). The activation enthalpy of 92.03 (kJ/mol) and activation entropy of – 31.42 (J/mol K) was obtained using plot of ln(k/T) vs. 1/T (Fig. 7b), where activation enthalpy has same order as the activation energy [21]. Gibbs free energy increases from -9.85 to – 4.32 (kJ/mol) with an increase in temperature (30-50 °C) (Fig. 7c). Thus spontaneity of the process increases with an increase in temperature [21]. Therefore, lycopene degradation/ isomerization in surfactant phase strongly depends upon the reaction media [21,22].

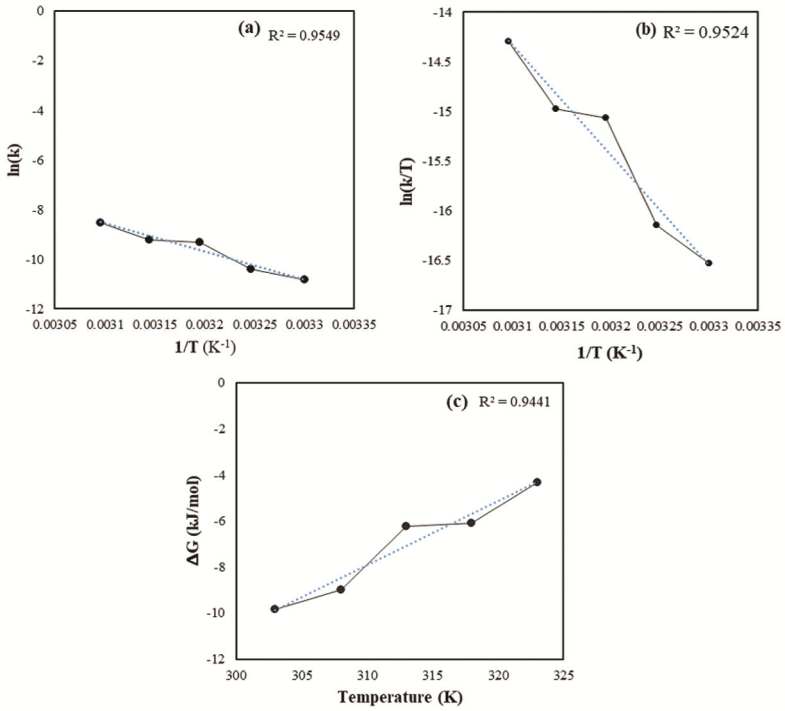

Fig. 7 — (a) Activation energy logarithmic plot ln(k) vs. (1/T), (b) activation enthalpy and activation entropy plot of ln(k/T) vs. (1/T) and (c) Gibbs free energy (Extract (Lycopene surfactant phase (L62)) = 1 mL, initial lycopene = 128.4 (mg/kg)), temperature = (30-50 °C), incubation time = (0-162 h)

Conclusion

Cloud point extraction of lycopene was successful. The effects of different operating factors on lycopene extraction such as surfactant concentration, lycopene concentration, temperature and time were investigated. Both adsorption isotherms were tested, and it was observed that Langmuir isotherm fitted the data. The linear form of the Langmuir model was used to determine Langmuir constants, k (0.057 mol/mol), and p (175.2 L/mmol) for the lycopene-L62 system. The established relationship between lycopene extraction and surfactant requirement was validated with experimental data. The PSO kinetic equation represented the adsorption of lycopene in coacervate phase. Results of thermodynamic parameters obtained show that the adsorption of lycopene in surfactant micelle is endothermic and spontaneous in nature. As per stability studies, a second order kinetic model better describes the lycopene degradation and the storage media had a significant impact.

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