

Effect of salts and surfactant and their doses on the gelation of extremely dilute solutions of methyl cellulose

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Abstract

The effect of different salts and surfactant and their doses on the gel temperature of extremely dilute solutions (below 1%) of methyl cellulose (MC) has been studied. The gel temperature decreases non-linearly (concave downward) with increase in MC concentration. The addition of salts like NaCl, $(\text{NH}_4)_2\text{SO}_4$ and $(\text{Na})_2\text{CO}_3$ lowers the gel temperature of MC due to its dehydration. But increase in gel temperature is also observed on addition of 0.5 and 1% NaCl to 0.6 and 0.7% MC solutions, respectively. The addition of 1% sodium carbonate causes appearance of clouds only up to 0.2% MC, cloudy gel followed by clear gel up to 0.3% MC, thereafter phase separation occurs even at room temperature. The effect of addition of a surfactant, sodium lauryl sulphate (SLS) on the process of gelation of aqueous MC solutions has been studied in detail. The gelation process depends on r , the ratio of weight% of surfactant and that of MC present in the aqueous solution. Gels are formed for the limit $0.02 < r < 0.1$ for all MC solutions, beyond which phase separation occurs. With increase in r (from the lower limit), gel temperature increases, reaches a maximum and then decreases. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Salts; Surfactant; Dilute solutions of methyl cellulose (below 1%)

1. Introduction

Methyl cellulose (MC) solutions in water set to a gel on warming up to a certain temperature and on cooling it reverts back to the sol state. This reversible sol–gel transition was first investigated by Heymann [1] and according to him the gelation is due to dehydration of hydrated MC molecules. Effort has been made to clarify the nature and structure of crosslinks present in thermoreversible MC gels. A group of scientists [2] came to the conclusion that the aggregation of MC molecules held together by dipolar force leads to gelation. Commercial MC is a heterogeneous polymer consisting of highly substituted zones called hydrophobic zones and less substituted ones called hydrophilic zones. MC is an alternative block co-polymer which consists of densely substituted hydrophobic and less substituted hydrophilic block sequences [3]. The hydrophobic parts are considered to form a structure of water around them and on raising temperature these water structures are disrupted. The densely substituted parts of MC form droplets, while the hydrophilic parts prefer to remain in water preventing coalescence of the droplets. Therefore, the droplets are actually described as ‘micelles’ and act as

‘crosslinking loci’. Rees [4] has suggested that the gelation of MC is due to liquid–liquid phase separation like micelle formation.

Gelation properties of MC can be substantially altered by the use of additives [5,6]. Most electrolytes depress the gel point owing to their greater affinity for water. This salting out by inorganic electrolytes was once believed as due to the competition between the polymer and the electrolyte for the water molecules. Solvent power of electrolyte solution depends strongly on both cations and anions, increasing with the polarisation of the anion. Stanton [7] studied a series of electrolytes in terms of solvent power of these aqueous salt solutions for non-electrolyte polymers.

The aggregation of surfactants and cellulose ether continues to be of special interest due to their industrial importance. This type of systems is found in fluids for enhanced oil recovery, paints, cosmetic applications and pharmaceutical compositions. Wang et al. [8] and Lindman et al. [9] studied in detail the gelation process for the cellulose ether and surfactant system in aqueous solution.

All the reported literature on gelation and phase separation of MC are in the concentration range of 1.0–2.5% of MC in water [1–4,10,11]. This paper reports the effect of salts and surfactants and their doses on the gelation

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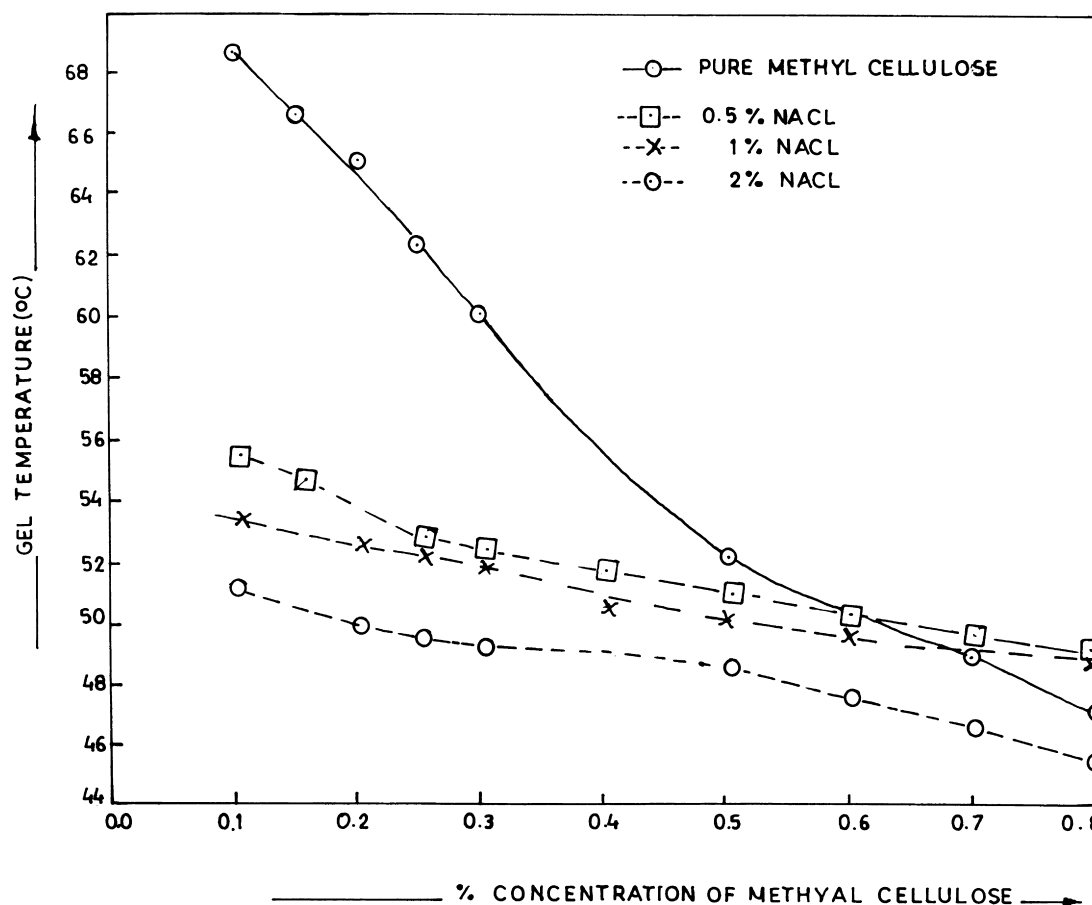


Fig. 1. Variation of gel temperature ($^{\circ}\text{C}$) with concentration (%) of MC for 0.5, 1 and 2% NaCl solutions and pure MC solutions (without NaCl).

and phase separation of MC solutions particularly at low concentration (below 1% MC in water).

2. Experimental

Methyl cellulose, Laboratory Grade in powder form was supplied by S D Fine-Chem Ltd., Biosar (India). Viscosity of 2% aqueous solution at 20°C as supplied by the manufacturer is about 400 cP. The weight average molecular weight of MC is 130,000 and its polydispersity index is 1.8. Its average degree of methyl substitution is 2.1. The aqueous solutions were prepared by dissolution of dried MC in demineralised water at 5°C during 24 h to assure a complete dissolution. The required amount of MC was dissolved to prepare solutions up to 0.8% concentrations. Below 1% concentration, the MC solution is an actual solution without any aggregates at low temperature [10].

3. Results and discussion

Fig. 1 shows the variation of gel temperature ($^{\circ}\text{C}$) against

% concentration of MC in the absence of any salt (pure MC solution) and in the presence of different concentrations of NaCl. With increase in MC concentration the gel point of pure MC solutions decreases. This lowering in gel temperature with increasing concentration of MC is not linear [10]. This may be explained as at very low concentration of MC, almost all the MC molecules (both less and high substituted) are linked to the water through intermolecular hydrogen bonding and the presence of less intermolecular hydrogen bonding between MC molecules leads to higher gelation temperature at low concentration. At higher concentrations the presence of more intramolecular hydrogen bonding compared to intermolecular hydrogen bonding between water and MC leads to a lowering of the gelation temperature. The gel temperature decreases with increase in methyl cellulose concentration for all NaCl solutions. The rate of decrease is much faster leading to a non-linear catastrophic fall in low concentration range (up to 0.4% MC), then the rate may either linearise or follow a plateau. This is due to high polar/electrolyte nature of NaCl, which is solubilised easily in water. The addition of NaCl to the methyl cellulose solutions greatly affect its gelation process. On the addition of a salt, the water molecules will be placed themselves around the cation of the salt, thus reducing intermolecular

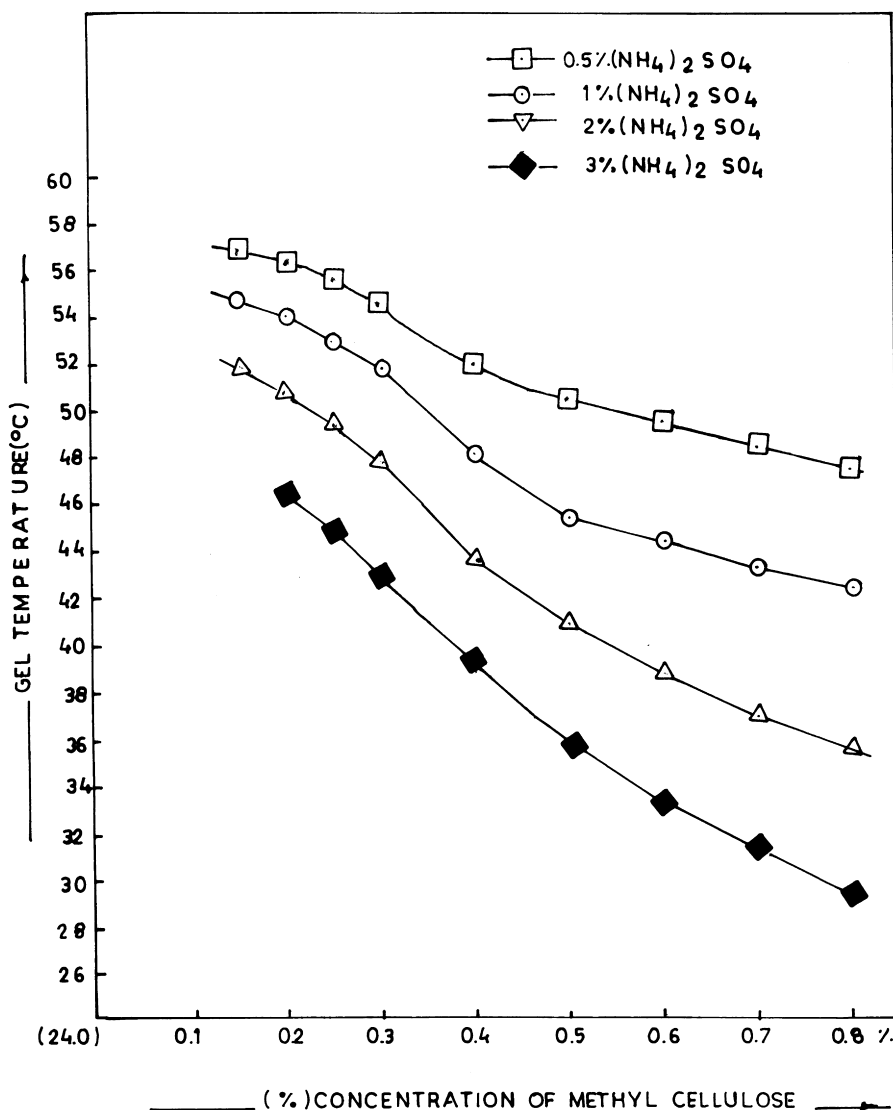


Fig. 2. Variation of gel temperature (°C) with concentration (%) of MC for 0.5, 1, 2 and 3% ammonium sulphate solutions.

hydrogen bond formation between water and hydroxyl group of methyl cellulose. This causes depletion of water layer leading to enhanced hydrophobe–hydrophobe interaction which ultimately leads to a lowering of the gelation temperature. The increase in MC concentration increases polymer entanglement leading to polymer–polymer interaction keeping the polymer–solvent interaction almost constant. For the extremely dilute solutions, the entanglement is minimum leading to the increase in gel temperature. But the presence of NaCl decreases gel temperature. These two opposing factors causes steep fall in the gap between the plots for pure MC and any NaCl salted MC. The same reasons also make these plots non-linear in the low concentration region up to 0.4% MC solution. Beyond this concentration, the plots are almost linear. The gel temperature increases on addition of 0.5 and 1% NaCl beyond the MC concentrations of 0.6 and 0.7%, respectively. This may be explained by the formation of macroscopic phase separation

(turbid gel) which has more thermodynamic stability leading to increase in gel temperature.

The variation of gel temperature with % concentration of MC in presence of different doses (0.5, 1, 2 and 3%) of ammonium sulphate are plotted in Fig. 2. From these plots it is evident that with increasing concentration of salt in same MC solution, gel temperature decreases. At low concentration up to 0.5% MC, all plots show non-linear decrease in gel temperature with increase in percent concentration of MC. At very low concentration below 0.5% MC the almost total decoiling occurs and increased polymer–water interaction causes an increase of the gelation temperature. Whereas the presence of salt-like ammonium sulphate which is a strong electrolyte, induces increased hydrophobic interaction leading to lowering of gelation temperature. Two opposing factors affect the gelation process enormously. At very low concentration of MC, the decoiling effect is more pronounced in comparison to the salting effect

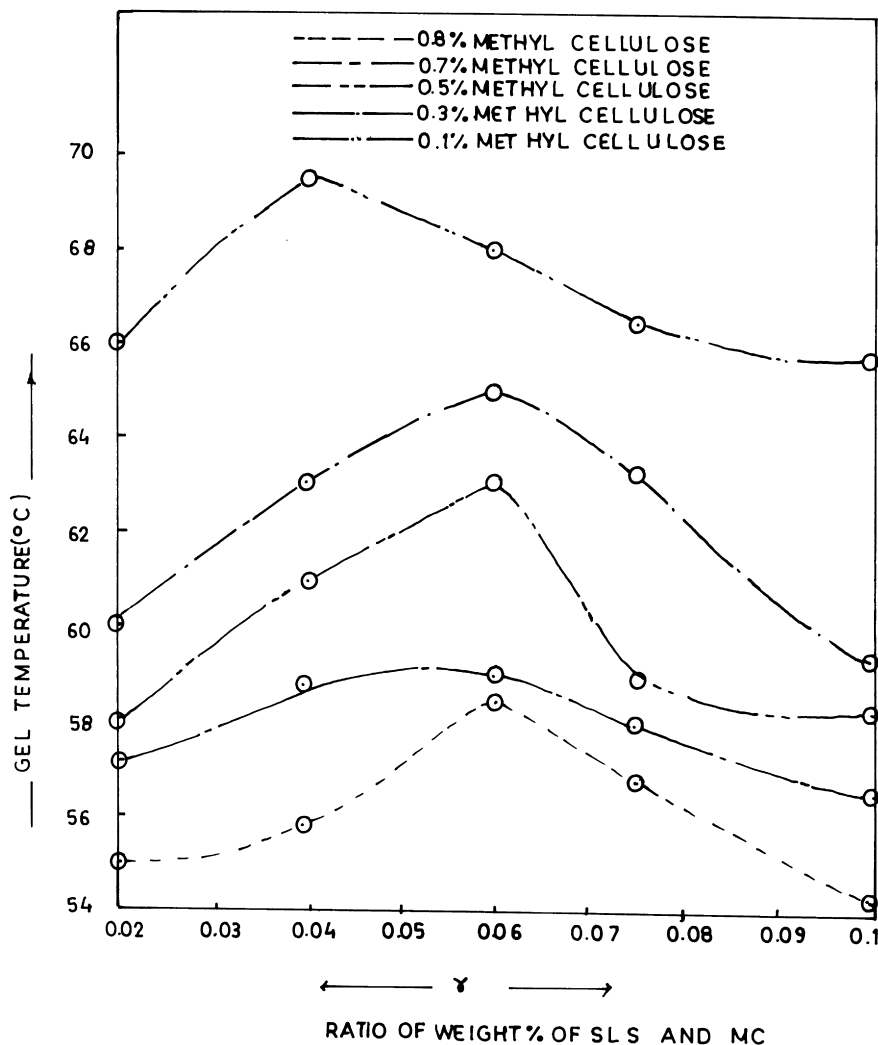


Fig. 3. Variation of gel temperature ($^{\circ}\text{C}$) with r (ratio of weight% of SLS and that of methyl cellulose) for 0.1, 0.3, 0.5, 0.7 and 0.8% of methyl cellulose.

of ammonium sulphate. Thus the rate of fall of gel temperature is much higher in this concentration region (up to 0.5% MC) leading to a catastrophic fall of gelation temperature around 0.5% MC. Beyond 0.5% MC almost all plots are linear due to the equal weightage of the two opposing factors.

The variation of gel temperature ($^{\circ}\text{C}$) with r (ratio of weight% of sodium lauryl sulphate (SLS) and that of MC) for fixed concentrations of MC (0.1, 0.3, 0.5, 0.7 and 0.8%) are plotted in Fig. 3. As the r values are taken at fixed concentrations of MC, so in other way these plots show the variation of gel temperature with change in SLS concentration. All the plots show similar increasing trend of gel temperature with increase in r up to a certain value of r ($r = 0.06$ for all cases except for 0.1% MC for which the gel temperature is maximum at $r = 0.04$). On attaining a maximum gel temperature, these plots show a decreasing trend in gel temperature with increase in r or SLS concentration. When $r > 0.1$, it is found that aqueous MC solutions show phase separation. Below $r = 0.02$, again phase separa-

tion occurs for all MC solutions. Nystrom et al. [12] have already reported that for a different surfactant (sodium dodecyl sulphate) and a different cellulose ether (ethyl hydroxy ethyl cellulose), thermal reversible gelation will occur in the approximate range of $0.02 < r < 0.1$. The above observed range of r is also true for the present system of SLS–methyl cellulose as is evident from the plot. SLS contains a long-chain surfactant anion, which attracts water molecules towards its end and can penetrate to a hydrophobe through its organic end. The lauryl sulphate anion helps in the interaction of hydrophobic part of MC with water molecules. On the basis of small angle neutron scattering experiments, it has been recently argued [13] that the structure of gels can be described by a mesh of polymer and surfactant ‘necklaces’ coexisting with lumps. The magnitude of these two structures vary with r and temperature. The formation of lumps is favoured at low values of r and high temperatures while high values of r and low temperatures promote the formation of necklaces made from SLS micelles collected by MC molecules. In a semi-dilute or dilute solution of MC

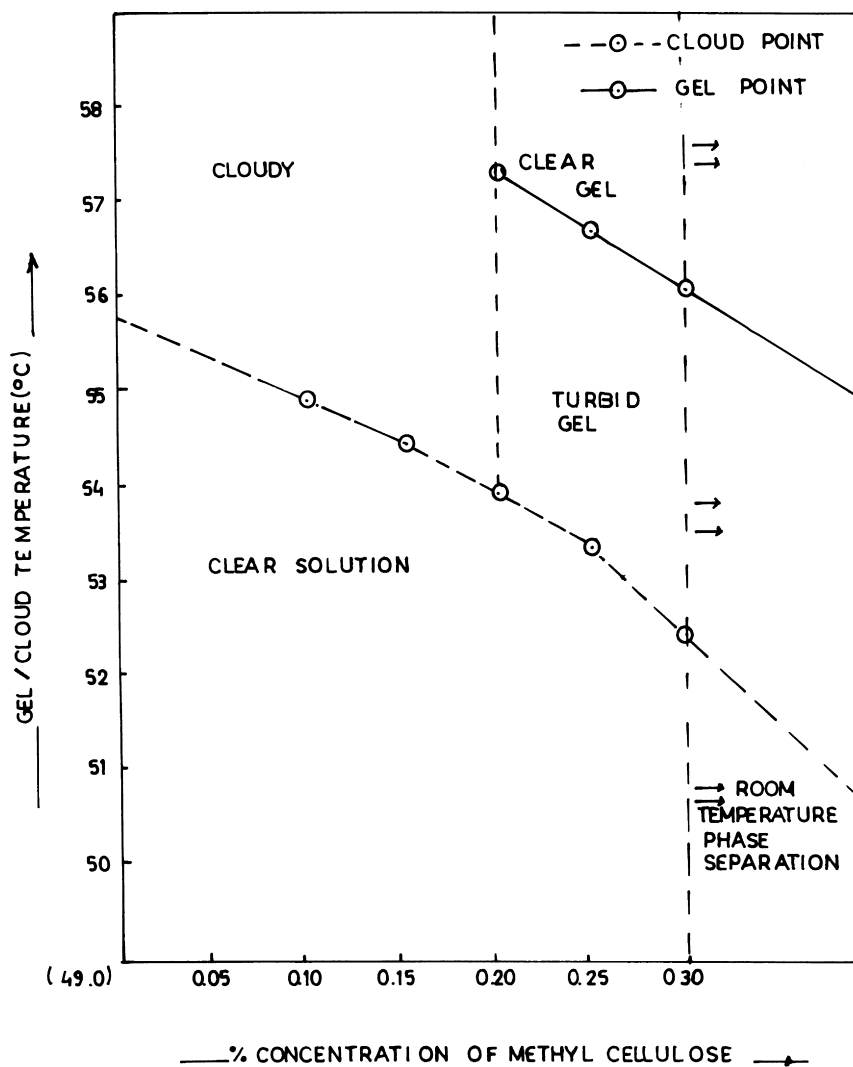


Fig. 4. Variation of gel temperature (°C) with concentration (%) of MC for 1% Na_2CO_3 solution.

in the presence of SLS, the delicate interplay between necklaces and lumps gives rise to an association of network leading to gelation. It is evident from the plots that gel temperature is maximum for a certain surfactant level. This indicates a delicate interplay of necklaces and lumps at this optimum value of r beyond which the lumps gradually break down and the structure of the solutes can be viewed as a mesh of overlapping necklaces. In this way, the number of effective micellar type crosslinks is reduced. This leads to the aggregation of necklaces which ultimately causes phase separation. According to the reports of Nystrom et al. [12], the maximum is shifted towards lower values of r with increase in concentration of cellulose ether. From Fig. 3, it is evident that r_{max} is almost constant at 0.6 for 0.3, 0.5, 0.7 and 0.8% MC solution but this is shifted towards a lower value of 0.4 for 0.1% MC solution. This shifting of the r value may be due to the fact that the value of critical aggregate concentration (CAC) of SLS decreases with increasing temperature [14].

At r values below 0.02, the solution becomes turbid (macroscopic phase separation) at elevated temperature. This may be due to the failure of interconnectivity condition because the formation of lesser number of micellar aggregates of SLS at $r < 0.02$ acts as a growth centre of lumps of MC. As the concentration of SLS approaches the critical aggregate value, the number of its micellar aggregate increases leading to the increased connectivity between aggregates of MC. On the other hand, the increasing concentration of SLS not only increases interconnectivity leading to gelation but also solubilises more MC through hydrophobe–hydrophobe interaction. These two opposing factors cause increase in gel temperature with increase in r up to r_{max} where the solubilisation efficiency of SLS becomes maximum.

The variation of gel and cloud temperature versus % concentration of MC in the presence of 1% sodium carbonate is shown in Fig. 4. The gel temperature plot is linear [10]. But below the concentration of 0.2% MC solution,

cloud of MC appears without any gelation. The cloud point plot is non-linear in nature (concave downward). A cloudy gel region separates the plots of the cloud and gel temperatures. The cloud point is lower than the gel point at same concentration of MC. It has been reported earlier [2] that the phase diagram of MC solution with temperature shows phase transition from clear solution to clear gel (up to 2 and beyond 7% solution) and to turbid gel (intermittent concentration of 2–7%). As we are studying the sol–gel transformation for concentrations below 1%, it is imperative that the solutions should form gels at higher temperature. Addition of salts like Na_2CO_3 not only reduces the gel temperature but also induces phase separation at certain concentrations. For very low concentrations of MC (up to 0.2%), it is evident that clear solution of MC transforms into a cloudy phase on increasing the temperature. The phase separation (clouds) and gelation are not separate phenomena. Due to increased hydrophobe–hydrophobe interaction, the MC solution transforms first to a cloudy phase on increase in temperature. This cloudy phase may persist depending upon the concentration of MC or it may lead to gel formation due to the formation of necklaces between small lumps formed by hydrophobe–hydrophobe interaction [12]. The lumps may grow to bigger size leading to clear phase separation. From the figure, it is evident that gelation occurs between 0.2 and 0.3% MC beyond which phase separation occurs on the addition of 1% Na_2CO_3 even at room temperature. This room temperature phase separation may occur due to critical MC concentration beyond which it helps in aggregation of the lumps on addition of hydrophilic Na_2CO_3 salt. The gelation is accompanied by turbidity in the concentration range of 0.2–0.3% of MC on increase in temperature. This is due to lower concentration of MC which allows formation of lumps and necklaces leading to turbid gel up to a certain temperature (gel temperature) beyond which formation of necklaces are regular between small lumps leading to clear gel. The formation of cloudy phase below 0.2% MC solution is due to the absence of interconnectivity as lesser number of micelles of MC are formed. These micelles aggregate to lumps due to hydrophobe–hydrophobe interaction causing phase separation with the appearance of cloudy phase.

4. Conclusions

The gel temperature decreases non-linearly (concave

downward) with increase in MC concentration. On addition of salts like NaCl and $(\text{NH}_4)_2\text{SO}_4$, the gel temperature curve maintains its non-linearity up to 0.4% MC beyond which these salts help its linearisation. On the other hand, this plot is linear on addition of 1% $(\text{Na})_2\text{CO}_3$ to the aqueous MC solutions. The addition of salts lowers the gel temperature of MC due to its dehydration. The addition of certain concentrations of salts like NaCl and Na_2CO_3 to specified concentration of MC leads to macroscopic phase separation (turbid gel) which leads to increase in gel temperature compared to pure MC solutions. The process of gelation occurs between certain level of surfactant which in turn is related to r (ratio of weight% of surfactant and that of MC). Gels are formed in the range of $0.02 < r < 0.1$ beyond which phase separation occurs. With increase in r , the gel temperature increases, reaches a maximum and then decrease. All these can be explained by the formation of lumps and necklaces (networking site) formed from the micelles of MC and SLS.

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