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Solution Behavior of Nonionic Polymer Hydroxypropylmethyl Cellulose: Effect of Salts on the Energetics at the Cloud Point

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ABSTRACT: The aim of the present work is to investigate the effect of various salts such as NaCl, KCl, NaBr, KBr, $NaNO_3$, Na_2SO_4, and Na_3PO_4 as additives on the phase behavior of nonionic polymer hydroxypropylmethyl cellulose, HPMC. The cloud point of HPMC has been found to be induced by the addition of above salts. On the basis of cloud point values obtained at different [HPMC], the energetics of the clouding process have been calculated. It was found that in the presence of salts the cloud point (T_{CP}) of HPMC decreased almost linearly with the salt concentration dependent on the type of salt used. Further, it was observed that the T_{CP} decreases on increasing HPMC concentration at a fixed salt concentration, followed by minima except for NaCl and Na_3PO_4 for which T_{CP} increases slightly after achieving a minimum value. Also, the free energy of clouding (ΔG_c) becomes less negative indicating that the process is becoming energetically less favorable on increasing the polymer concentration.

INTRODUCTION

Water-soluble polymers play an important role in the pharmaceutical and petroleum industries.[1,2] These polymers exhibit clouding upon heating their solution. The clouding process can be influenced by additives, and both delay and enhancement by them has been reported in the literature.[3−16] An understanding of the cloud-point phenomena is of both practical and theoretical interest under varied thermal conditions.[17] The current explanation of the cloud point is that, when the cloud point approaches, an increased intermicellar interaction is the result of strong entropy dominance. As the temperature rises, the hydrogen bonding gets diminished and the polymer solubility becomes less and thus phase separation may occur. At the T_{CP}, the polymer precipitates out of solution as a consequence of equal chemical potentials between the two phases, one richer in polymer, of solute and solvent, respectively. Thus, T_{CP} provides a simple and powerful tool for qualitative characterization of the polymer thermodynamics in systems with LCST (lower critical solubility temperature) behavior and their interactions with low molecular weight amphiphiles. The phase behavior of cellulose ethers can easily be tuned with the help of suitable additives. Several cellulose derivatives, like HPMC, is distinguished by mixed hydrophobic and hydrophilic structural units. Thus, the understanding of phase behavior of HPMC including the effects of salts on T_{CP} has become quite important. At the cloud point, the increase in entropy is much more negative than that arising from the repulsive forces. Hence, the total free energy is negative and the T_{CP} appears. The influence of an additive on the T_{CP} depends on how it affects the intermicellar interactions.[18] Many theories are reported in the literature to explain the presence of cloud point, but this problem still remains to be understood. Further the effect of different types of salts on the same system (polymer) was not discussed earlier.

This paper reports how a series of additives (salts) affects the T_{CP} of aqueous solution of nonionic polymer, HPMC. The additives investigated in the present work include some trivalent, divalent and mononvalent salts namely NaCl, KCl, NaBr, KBr, $NaNO_3$, Na_2SO_4, and Na_3PO_4.

EXPERIMENTAL SECTION

Hydroxypropylmethyl cellulose (HPMC; mol wt 10 000, hydroxylpropyl content ~ 0.09 mass fraction, Fluka, Switzerland), sodium chloride (NaCl; Merck, Germany), sodium bromide (NaBr; s.d.fine-CHEM Limited, India), potassium chloride (KCl; Merck, Germany), potassium bromide (KBr purified; E. Merck, India), sodium nitrate purified ($NaNO_3$; E. Merck, India), sodium sulfate anhydrous (Na_2SO_4; HIMEDIA, India), and trisodium phosphate dodecahydrate GR (Na_3PO_4; Merck, India) were used as received. Double distilled water of specific conductance 1 to 2 $\mu S \cdot cm^{-1}$ was used to prepare all of the polymer solutions. The concentration of HPMC has been expressed in $mol \cdot kg^{-1}$.

Cloud Point (T_{CP}) Determination. Freshly prepared stock solutions (containing HPMC with or without different salts) were used to obtain samples for cloud point (T_{CP}) measurements. The experimental procedure for T_{CP} measurements has earlier been detailed.[5,6,19,24] In the actual experiments, the solution was taken in a stoppered test tube and was securely placed in a heating bath with constant stirring and a controlled increment of heat. The point of clouding or turbidity was visually observed and was noted at the start of the phenomenon. The heating was then stopped, and the system under condition of stirring was allowed to slowly cool. The temperature for the disappearance of turbidity was also noted. The mean value of the two temperatures was considered as the T_{CP} of the system. The measured T_{CP} was accurate within ± 1 %.

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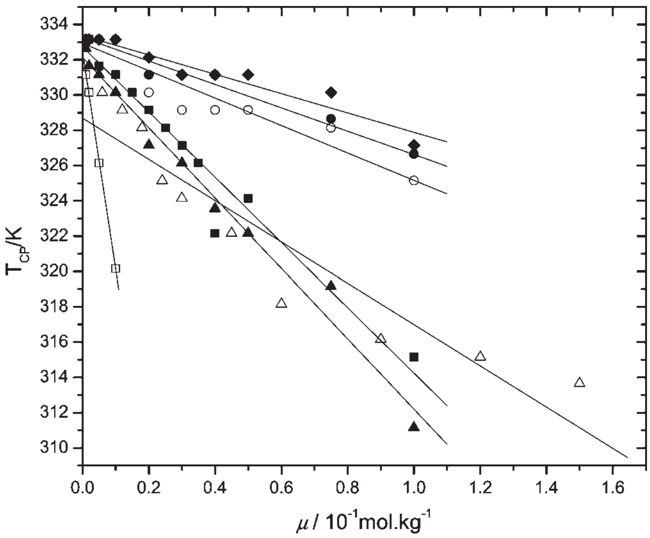

Figure 1. T_{CP} vs μ profiles for HPMC (1×10^{-3} mol·kg^{-1}) in presence of salts. ■, NaCl (18.4); ●, NaBr (6.6); ▲, KCl (19.9); ○, KBr (7.7); ♦, $NaNO_3$ (5.4); Δ, Na_2SO_4 (11.7); □, Na_3PO_4 (123.4). Values in parentheses are slopes of the related plots.

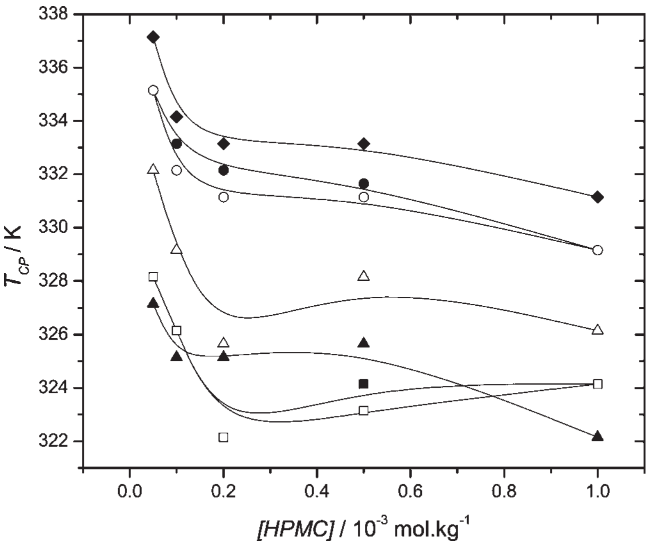

Figure 2. Dependence of T_{CP} on [HPMC] in presence of salts. ■, NaCl (0.515 mol·kg^{-1}); ●, NaBr (0.527 mol·kg^{-1}); ▲, KCl (0.519 mol·kg^{-1}); ○, KBr (0.531 mol·kg^{-1}); ♦, $NaNO_3$ (0.522 mol·kg^{-1}); Δ, Na_2SO_4 (0.0503 mol·kg^{-1}); □, Na_3PO_4 (0.0509 mol·kg^{-1}).

■ RESULTS AND DISCUSSION

1. Salt-Effect and Clouding. When the solution of pure HPMC (1×10^{-3} mol·kg^{-1}) is heated, phase separation occurs at about 333.15 K; this means that below 333.15 K the HPMC molecules are surrounded by a network of water molecules and, at higher temperature, entropy destroys the network and phase separation occurs due to the weak van der Waal's attraction between the HPMC molecules.[20] A large number of electrolytes of different valences were tried at different concentrations to check the stability or phase separation (i.e., clouding) of HPMC by the effect of temperature. All of the salts under study (NaCl, NaBr, KCl, KBr, $NaNO_3$, Na_2SO_4, and Na_3PO_4) were found to initiate or induce clouding of HPMC. The results are presented in Figure 1 at 1×10^{-3} mol·kg^{-1} of HPMC. The plots are in terms of ionic strengths (μ, in mol·kg^{-1}) and they followed the efficiency sequence of Na_3PO_4 ($\mu = 0.01-1.5$) > Na_2SO_4 ($\mu = 0.01-0.1$) > KCl ($\mu = 0.01-1.0$) > NaCl ($\mu = 0.01-1.0$) > KBr ($\mu = 0.01-1.0$) > NaBr ($\mu = 0.01-1.0$) > $NaNO_3$ ($\mu = 0.01-1.0$). It can be seen that the T_{CP} values for NaCl, NaBr, KCl, $NaNO_3$, and Na_3PO_4 decrease almost linearly with the increasing molar concentration of the salt, which is termed as salting out-effect. However, for other salts, such as KBr and Na_2SO_4, the curve is slightly convex toward the ionic strength (*X* axis). This is due to the fact that the change in T_{CP} with ionic strength (μ) depends somewhat on the choice of electrolytes and their concentrations as reported by Schott et al.[5] The sequence revealed that the di- and trivalent anions show better efficiency than the monovalents at much lower molar concentration. The reduction of T_{CP} per unit ionc strength found from the slopes of the straight-line plots were 123.4, 19.9, 18.4, 11.7, 7.7, 6.6, and 5.4 for Na_3PO_4, Na_2SO_4, KCl, NaCl, KBr, NaBr, and $NaNO_3$ respectively. Similar results were reported by Abhijit Dan et al.[21] It is sometimes difficult to determine how the salt affects the cloud point according to the above order, because the effect of salts on the clouding of nonionic polymer should be correlated to the effects of anions and cations. It was seen that the anions generally raise or lower the T_{CP} more than cations. The previous study[22] shows that the kosmotropic anions cause a salting-out effect by destabilizing the H bonds between water and the polar groups of the polymer and by increasing the cost of hydration, resulting in a linear decrease in T_{CP} with increasing salt concentration. In addition, chaotropic anions can also cause a slight salting-out effect by increasing the hydrophobic hydration. Alternatively, the anions themselves are hydrated and compete with the polymer for water of hydration. Lowering the T_{CP} by the alkali metal cations (Na^+ and K^+) resulted from the dehydration of polymer due to the competition for water of hydration by cations. The above explanation may be ascribed as purely speculative as also reported in the literature by earlier investigators.[21,22]

Any change in T_{CP} of a polymer/water system on the addition of the third component such as surfactant or salt can be ascribed to the variation of the hydrophobic/hydrophilic balance in the system and, as a result, modification of the interaction.[23,24] It is evident from Figure 1 that addition of small amount of salt causes the T_{CP} to decrease due to the beginning of the increased interaction between HPMC and salt. It is supposed that the decrease in T_{CP}, on addition of salt, is only obtained when an electrolyte is present. The T_{CP} change of the polymer on addition of salt is governed by a delicate balance between electrostatic effects and hydrophobic interactions. In HPMC, the additives (i.e., salts) effect on its stability is not drastic. Dehydration of HPMC by temperature and water abstraction by salts acted concertedly toward the instability of the polymer to result clouding. Highly hydrated salts,[25−28] like Na_3PO_4 and Na_2SO_4, assisted efficient clouding of HPMC at lower ionic strength than weakly hydrated salts,[27] like NaCl, KCl, KBr, NaBr, and $NaNO_3$. NO_3^- ion has only a low tendency for salting-in or salting-out.

2. Dependence of T_{CP} on HPMC Concentration. The dependence of T_{CP} on [HPMC] for NaCl (0.515 mol·kg^{-1}), NaBr (0.527 mol·kg^{-1}), KCl (0.519 mol·kg^{-1}), KBr (0.531 mol·kg^{-1}), $NaNO_3$ (0.522 mol·kg^{-1}), Na_2SO_4 (0.0503 mol·kg^{-1}), and Na_3PO_4 (0.0509 mol·kg^{-1}) is shown in Figure 2. It can be seen that T_{CP} for KCl, KBr, NaBr, $NaNO_3$, and Na_2SO_4 decreases on increasing [HPMC] and reaches a minimum value at around 0.002×10^{-3} mol·kg^{-1}, and then it

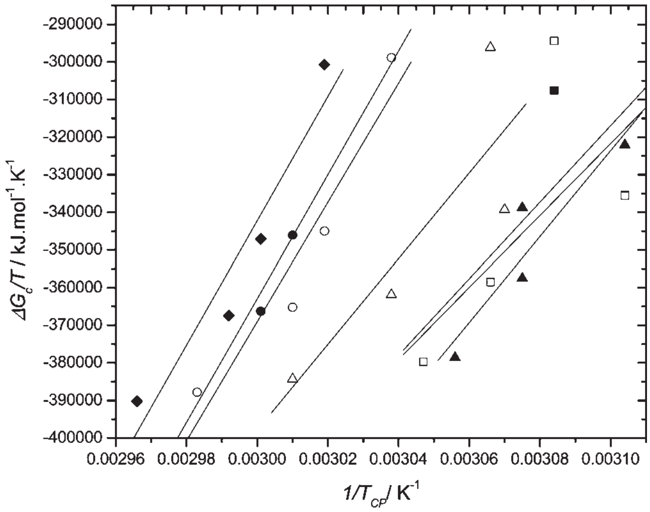

Figure 3. $\Delta G_c/T_{CP}$ vs $1/T_{CP}$ plots at fixed [salts]. ■, NaCl; ●, NaBr; ▲, KCl; ○, KBr; ◆, $NaNO_3$; △, Na_2SO_4; □, Na_3PO_4.

increases slightly up to the concentration of around 0.005×10^{-3} mol·kg^{-1} and again decreases, but for NaCl and Na_3PO_4 it increases after 0.005×10^{-3} mol·kg^{-1}. Almost similar results were reported in the earlier investigations.[21]

With the consideration of clouding as the point of phase separation (or the solubility limit), the free energy of phase separation or clouding (ΔG_c) was calculated from eq 1 as given below:

$$\Delta G_c = RT_{CP} \ln X_{HPMC} \qquad (1)$$

where X_{HPMC} is the mole fraction concentration of HPMC at T_{CP} and R is the gas constant (8.314 J·K^{-1}·mol^{-1}). The slopes of the linear (least-squares) plots between ($\Delta G_c/T_{CP}$) versus ($1/T_{CP}$) (Figure 3), as per eq 2, were then used to obtain the ΔH_c values

$$d(\Delta G_c/T_{CP})/d(1/T_{CP}) = \Delta H_c \qquad (2)$$

Thereafter, the Gibbs−Helmholtz equation (eq 3) was used to calculate the entropy changes

$$\Delta S_c = (\Delta H_c - \Delta G_c)/T_{CP} \qquad (3)$$

The ΔH_c, ΔG_c, and ΔS_c values thus obtained are collected in Table 1. The values were high as was observed for other clouding compounds earlier studied.[4−6] Among the effective cloud forming salts, ΔH_c followed the order NaBr > $NaNO_3$ > KCl > KBr > Na_2SO_4 > Na_3PO_4 > NaCl in the present study. The ΔH_c values of NaBr, KCl, KBr, and $NaNO_3$ were around 2-fold as was observed for NaCl, Na_2SO_4, and Na_3PO_4. Almost similar results were obtained by earlier investigators.[3−5]

The T_{CP} of HPMC decreases on increasing its concentration at a fixed salt concentration, and ΔG_c becomes less negative (indicating that the clouding is becoming energetically less favorable on increasing the concentration of the polymer). The system becomes slightly more ordered on increasing the polymer as indicated by a decrease in the entropy of all of the systems used in the study.

The ΔS_c values were all large and positive. The high positive entropy suggests loose, disorderly, and desolvated HPMC assemblies in solution. Desolvation of the polymer makes a major contribution to the positive entropy change.

Table 1. Cloud Point (T_{CP}) and Energetic Parameters for Clouding at Various Concentrations of Hydroxypropylmethyl Cellulose (HPMC) Solutions in the Presence of Different Salts (Sodium Chloride (NaCl), Sodium Bromide (NaBr), Potassium Chloride (KCl), Potassium Bromide (KBr), Sodium Nitrate ($NaNO_3$), Sodium Sulfate Anhydrous (Na_2SO_4), and Trisodium Phosphate Dodecahydrate (Na_3PO_4)

HPMC 10^{-3}	T_{CP}	ΔG_c	ΔH_c	$T\Delta S_c$
mol·kg^{-1}	K	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}
NaCl (0.515 mol·kg^{-1})				
0.05	328.15	−38.0	195.3	233.3
0.10	326.15	−35.9		231.2
0.20	322.15	−33.6		228.9
0.50	324.15	−31.3		226.6
1.00	324.15	−29.4		224.7
NaBr (0.527 mol·kg^{-1})				
0.05	335.15	−38.8	486.1	234.1
0.10	333.15	−36.6		231.9
0.20	332.15	−34.6		229.9
0.50	331.65	−32.0		227.3
1.00	329.15	−29.9		225.2
KCl (0.519 mol·kg^{-1})				
0.05	327.15	−37.9	470.2	233.2
0.10	325.15	−35.8		231.1
0.20	325.15	−33.9		229.2
0.50	325.65	−31.5		226.7
1.00	322.15	−29.3		224.6
KBr (0.531 mol·kg^{-1})				
0.05	335.15	−38. 8	465.4	234.1
0.10	332.15	−36.5		231.8
0.20	331.15	−34.5		229.8
0.50	331.15	−32.0		227.3
1.00	329.15	−29.9		225.2
$NaNO_3$ (0.522 mol·kg^{-1})				
0.05	337.15	−39.0	471.0	234.3
0.10	334.15	−36.7		232.0
0.20	333.15	−34.7		230.0
0.50	333.15	−32.2		227.5
1.00	331.15	−30.1		225.4
Na_2SO_4 (0.0503 mol·kg^{-1})				
0.05	332.15	−38.4	313.3	233.7
0.10	329.15	−36.2		231.5
0.20	325.65	−33.9		229.2
0.50	328.15	−31.7		227.0
1.00	326.15	−29.6		224.9
Na_3PO_4 (0.0509 mol·kg^{-1})				
0.05	328.15	−38.0	306.3	233.3
0.10	326.15	−35.9		231.2
0.20	322.15	−33.6		228.9
0.50	323.15	−31.2		226.5
1.00	324.15	−29.4		224.7

■ CONCLUSIONS

The effects of various salts such as NaCl, KCl, NaBr, KBr, $NaNO_3$, Na_2SO_4, and Na_3PO_4 as additives was seen on the cloud point (T_{CP}) of the nonionic polymer HPMC. It was found that in the presence of these additives the T_{CP} of HPMC decreases almost linearly on increasing their molar concentration (salting-out effect) either by dehydration or by enhancing the structuring of water. Trivalent and divalent anions show higher efficiencies than monovalent anions at much lower molar concentrations. The dependence of T_{CP} on HPMC concentration at a fixed salt concentration was also studied and it was found that, as HPMC concentration increases, T_{CP} initially decreases and then increases, except in the case of KCl and Na_2SO_4. As [HPMC] increases, ΔG_c becomes less negative indicating that the clouding is becoming energetically less favorable on increasing the polymer concentration. The present results can be exploited in petrochemical, pharmaceutical, and other formulations as HPMC is an important ingredient in all these industries.

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