

Studies on Surface Tension of Poly(Vinyl Alcohol): Effect of Concentration, Temperature, and Addition of Chaotropic Agents

A. Bhattacharya, P. Ray

Reverse Osmosis Division, Central Salt and Marine Chemicals Research Institute, Bhavnagar, Gujarat, India

Received 30 September 2003; accepted 16 December 2003

DOI 10.1002/app.20436

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: It is generally considered that the H-bonds are responsible for the stabilization of network of PVA in water. The major types of intermolecular interactions from inorganic salts are responsible for the network of poly(vinyl alcohol) (PVA) and water, which ruptures the multiple H-bonds between the -OH groups of the polymer chains; therefore, various ions possessing abilities to affect these bonds result in salting out. It has been suggested that water molecules in the region of ionic hydration spheres must have strong orientation preferences, which could considerably restrict their ability to reorient and form hydration

shells around nearby nonpolar solutes and thus affect the microstructure. In this article, our primary objective was to study the variation of surface tension, as it reflects the change in short-range forces. Apart from this, we have also studied the surface tension behavior with the variation of concentration and temperature for different molecular weights of PVA. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 122–130, 2004

Key words: water-soluble polymers; surfaces; association; solution properties

INTRODUCTION

To the separation scientists, the combination of solubilizing properties of the water-soluble polymer molecules and inorganic salts is an interesting area in the field of extraction and fractionation.^{1,2} Several liquid-phase extraction technologies employing phase-forming polymers in aqueous solution have the potential to replace volatile organic compounds in classical solvent extraction technologies. In this connection, we have chosen poly(vinyl alcohol) (PVA), as it is well known for its interesting behavior and its versatile applications.³ In water, there exist two possible intermolecular interactions among PVA chains or between PVA and water, as follows: (1) H-bonding between modified hydroxyl groups on PVA chains and (2) H-bonding between the -OH groups of PVA and water molecules.

As short-range forces are as important in determining the effect of particular salts on nonelectrolyte solution behavior as long-range electrostatic forces, the study of surface tension is very important. Surface tension arises from the geometrical unbalance of the force fields acting on the molecules in the interface. The molecule itself is interesting in a structural bonding point of view, as well as its geometry, considerably

longer than its width, and the study of surface tension will be quite effective in partitioning of aqueous biphasic systems.^{4,5} The water-mediated interactions of polymer molecules and salt ions are sensitive to the solute size and shape, ion charge density, and salt concentration.^{6,7}

In this article, we have concentrated our studies regarding surface tension mainly on the following three aspects: (1) chemical nature and concentration of the surface-active polymer of different molecular weight; (2) temperature; and (3) effect of addition of chaotropic agents to the PVA solution of different molecular weights.

EXPERIMENTAL

PVAs of different molecular weights (14,000, 125,000 and 72,000) are procured from SD Fine Chemicals (India) and Aldrich. For all solutions, distilled water purified in a Millipore water purifier (Milli-Q-gradient) is used. All the other reagents are of laboratory grade. The measurements are made with the Dynamic Contact Angle Tensiometer (DCAT 21), from Data-physics. Aqueous solutions of PVA 0.001 to 0.3% (W/V) are taken for the present study.

RESULTS AND DISCUSSION

Variation of surface tension with concentration

The surface tension of a system is governed by the usual thermodynamic variables and primarily by the

Correspondence to: A. Bhattacharya (bhattacharyaamit1@rediffmail.com).

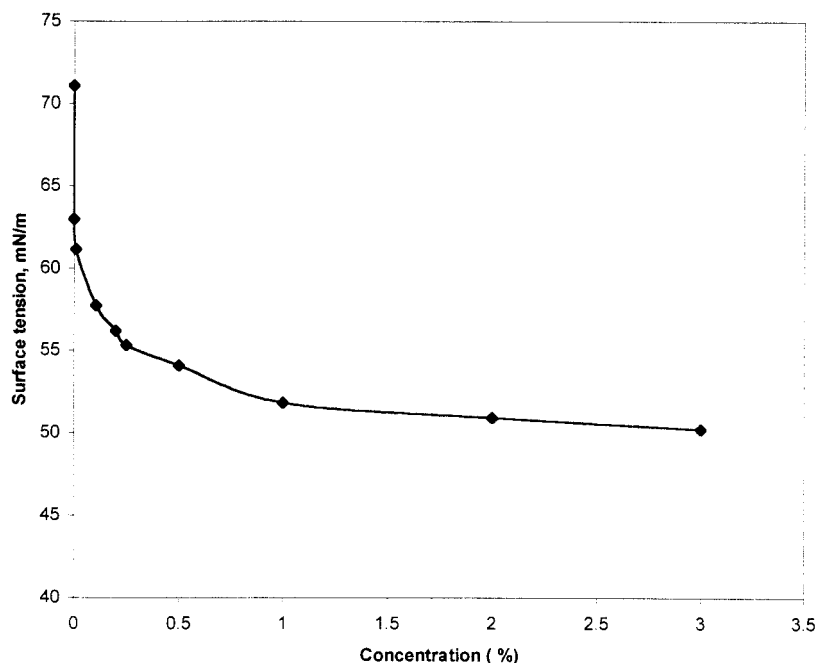


Figure 1 Variation of surface tension of PVA, M_w 72,000 with concentration.

chemical nature of the components present in the surface phase. Because of the presence of —OH groups, PVA has the capability of H-bonding with its solvents and decreases their surface tension as other surface-active agents.^{8–10} The surface activity phenomenon is qualitatively explained from its molecular picture (i.e., the nature of its monomeric unit, its orientation, and overall distribution in solvent medium as well as interaction with the solvent molecules). For PVA solutions, both species, PVA (solute) and water molecules, are free to migrate and exert attractive forces of attraction on their immediate neighbors. Because of the basic difference in their structure and relative interaction with the neighboring molecules in the solution, the fields of attractive forces exerted by the PVA molecules will be different from those exerted by water molecules. In the bulk solution, PVA molecules remain at a higher free-energy state because of the large association tendency of water molecules among themselves through H-bond. Hence, PVA always has a tendency to migrate from bulk to the surface (i.e., at a low free-energy state). The statistical accumulation in the surface of those molecules with weaker fields results in a lowering of surface-free energy. It can be also correlated with the Gibb's adsorption equation:

$$\Gamma = - \frac{cd\gamma}{RTdc}$$

(Considering the activity coefficient is unity)

The accumulation of PVA on the surface results in excess positive surface tension values; hence, the sur-

face tension of the PVA solution will be decreased. With the increase in concentration of PVA, the surface excess value will be increasing, and thus, the surface tension trend will be reversed.

Figure 1 shows that there is a decrease in surface tension with concentration, and no maxima or minima is observed. At low concentration, the decrease is very sharp; then, the curve levels off and continues to fall slowly as the concentration increases. Here, it has been observed that the decreasing trend is rather low in the high-concentration range (>0.25%). At low concentration of PVA (<0.25%), the attraction among the water molecules results in a water-pulling effect. Here, the inward attraction of water molecules from the surface to the bulk is greater than that in a PVA solution of higher concentration. Hence, an appreciable enhancement to the surface excess value results.

The concentration dependence of the surface tension values are being studied for the different molecular weights of PVA, and it follows the same trend for the different molecular weights of PVA studied. Here, we have presented the variation of surface tension values for the PVA (0.001 to 3%), of molecular weight 72,000.

Effect of temperature

The surface tension of solutions decreases with an increase in temperature. With the increase in temperature, heat is absorbed, and as a result, surface is extended. This heat represents the work necessary to pull the new molecules into the surface against the

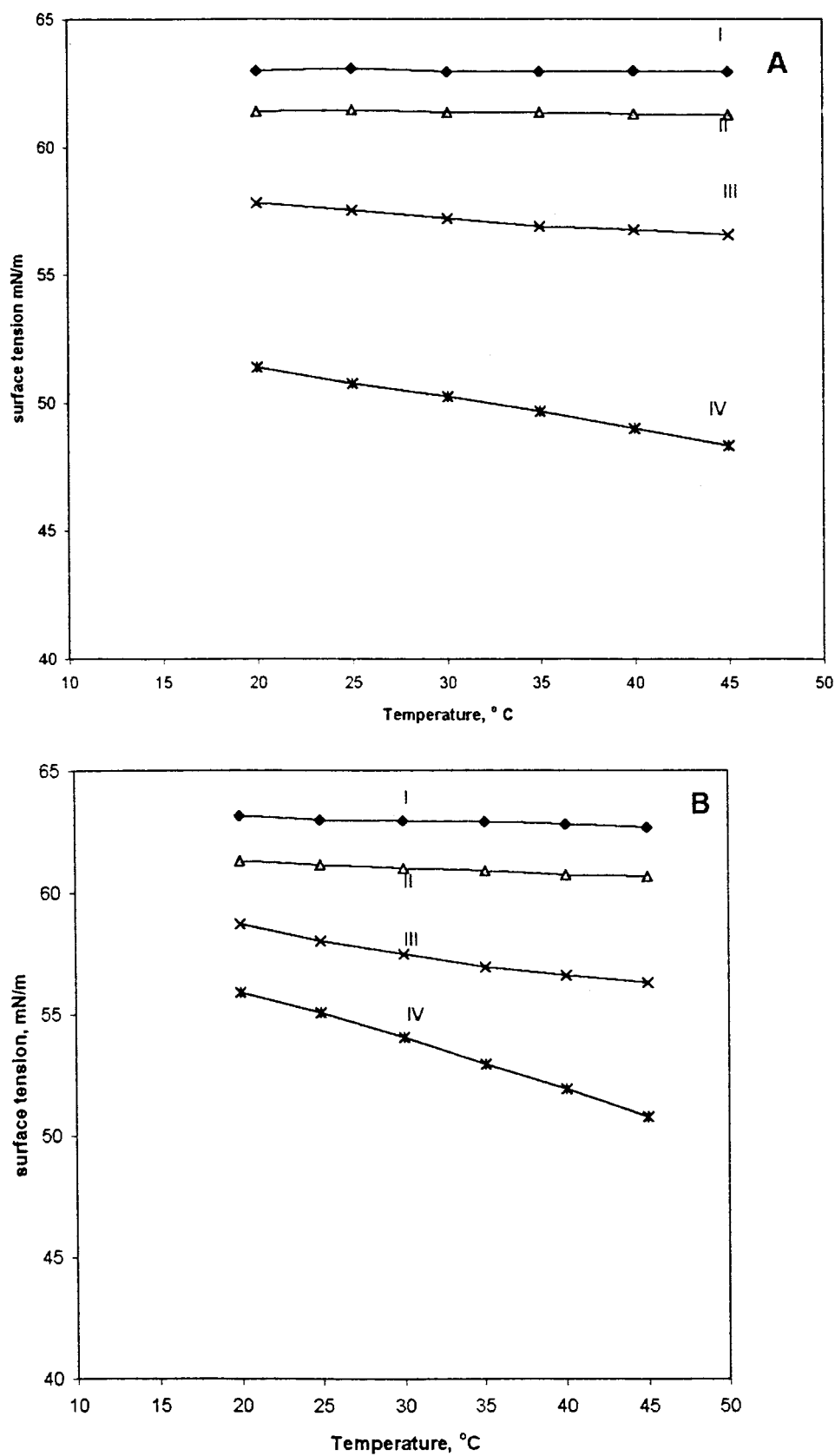


Figure 2 Variation of surface tension of PVA with temperature: A (M_w 14,000), B (M_w 72,000), C (M_w 125,000); (I) 0.001%, (II) 0.01%, (III) 0.1%, and (IV) 0.25%.

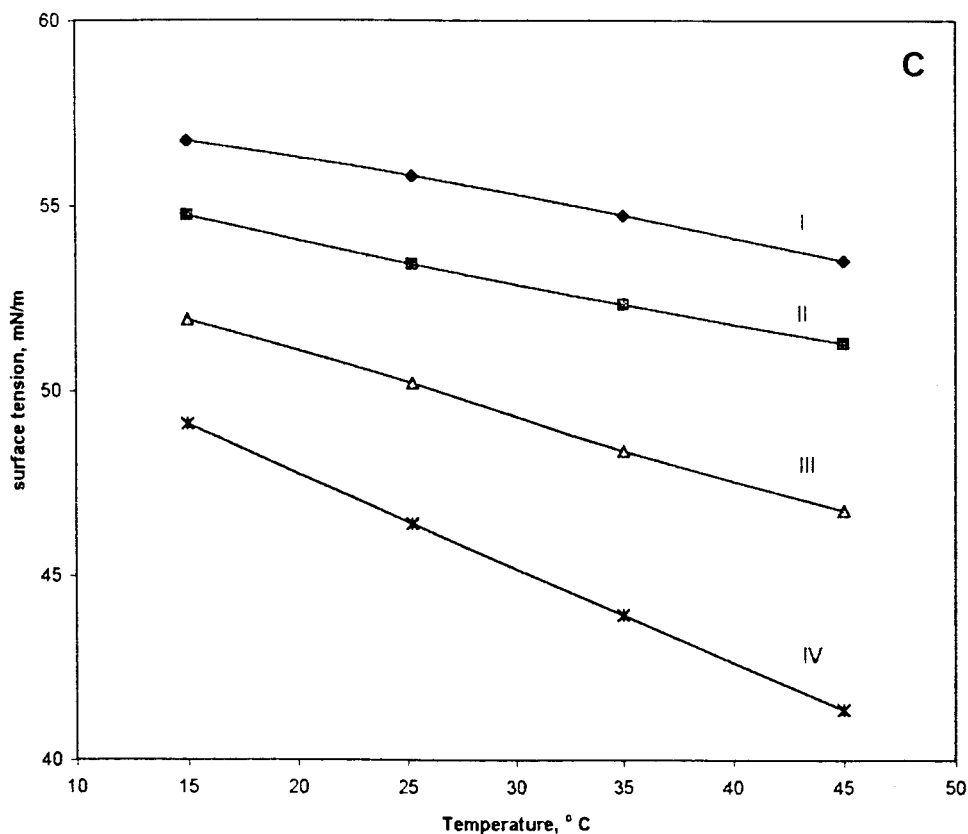


Figure 2 (Continued from the previous page)

attractive forces of the interior. Thus, enrichment of the surface occurs. The variation of the surface tension with the temperature is shown in Figure 2(A–C) for the different molecular weights of PVA. It was seen that, with the increase of temperature, the surface tension decreases. It is interesting to mention that, with the increase of concentration, the slope of the line increases, which means the temperature effect is more pronounced; as in the case of higher concentration, the surface enrichment predominantly occurs. The same trend is observed in the case of PVA of all the molecular weights we have studied (e.g., 14,000, 72,000, and 125,000).

Effect of addition of salts to the PVA solution

In general, hydrophilic polymeric solution (e.g., PVA) in the presence of salt does not coagulate with the addition of small quantities of electrolyte. Considerable quantities of electrolyte solution added to the polymeric solution cause the polymer to separate out from the polymer-rich phase. The fact is often called salting out. In this case, the coagulation may take place in such a way that the two liquid phases are formed: one is polymer-rich with a small amount of electrolyte and the other one is electrolyte-rich with a small amount of polymer. De Jong and Kruyt have called

this particular type of coagulation process coacervation.¹¹ The conventional view of salting out is based on the competition of water of hydration between the polymer and salt molecules. This causes the loss of water hydration of the polymer molecules and thus decreases the solubility in the electrolyte-rich phase. More recently, it has been shown that in the presence of chaotropic ions (e.g., Cl^- , SO_4^{2-} , etc.) the disruption of tetrahedral structure of water occurs.^{12,13} The salts affect the orientational order on the water that is incompatible with that of the directional hydrogen bonds of the solute displaying a miscibility gap.² From the neutron diffraction data, Leberman and Soper¹² suggest that a similar kind of disordering mechanism occurs in aqueous solution of ionic salts of different types, but the size of the effect depends significantly on the particular ions involved (i.e., the structural change is ion-specific). They have shown that SO_4^{2-} ions are more effective than Cl^- ions in the disruption of tetrahedral structure of water. The change in structural function is as if the pressure of the water has been increased. In the present case, we are interested in the effect of surface tension on addition of chloride and sulfate ion, as the anion appears to dominate the phase separation.¹⁴ At constant temperature, the pressure effect of the water is different for the different salts. The effect of NaCl addition to the PVA solution

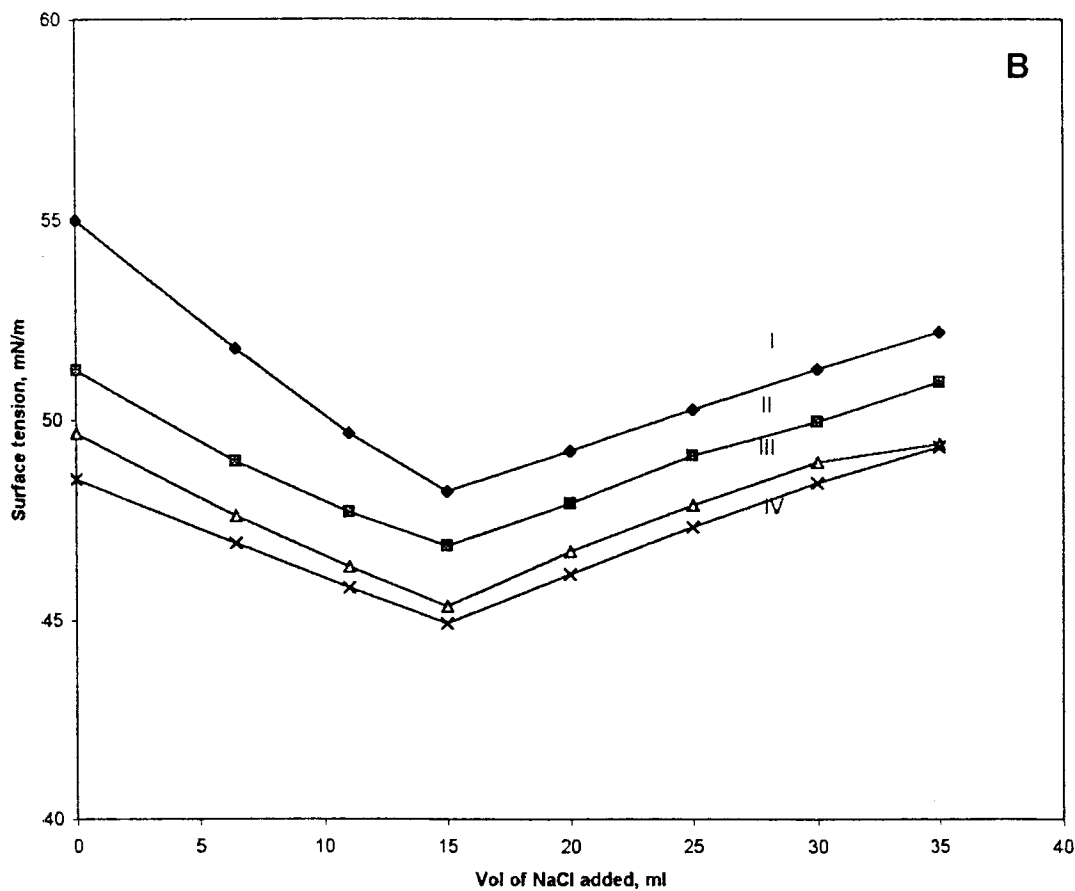
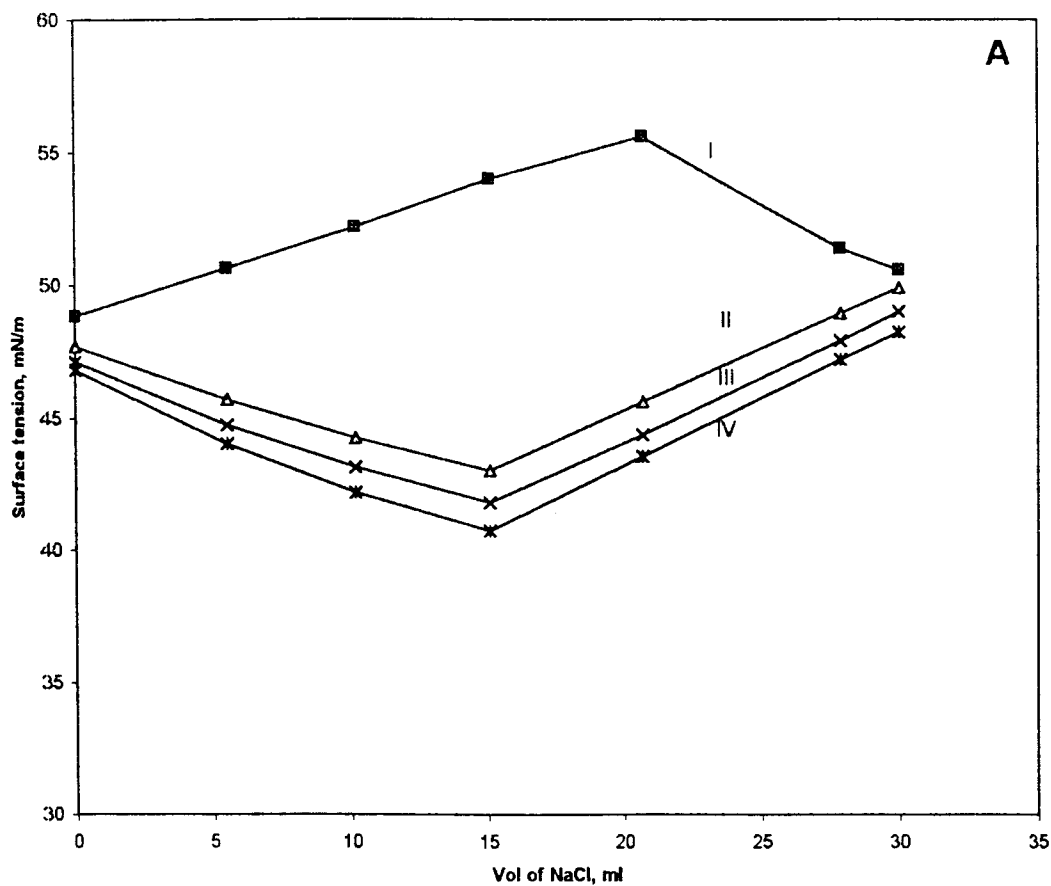


Figure 3 Effect of surface tension on addition of 30% NaCl solution to PVA, A (M_w 14,000), B (M_w 72,000), C (M_w 125,000); (I) 0.001%, (II) 0.01%, (III) 0.1%, and (IV) 0.25%.

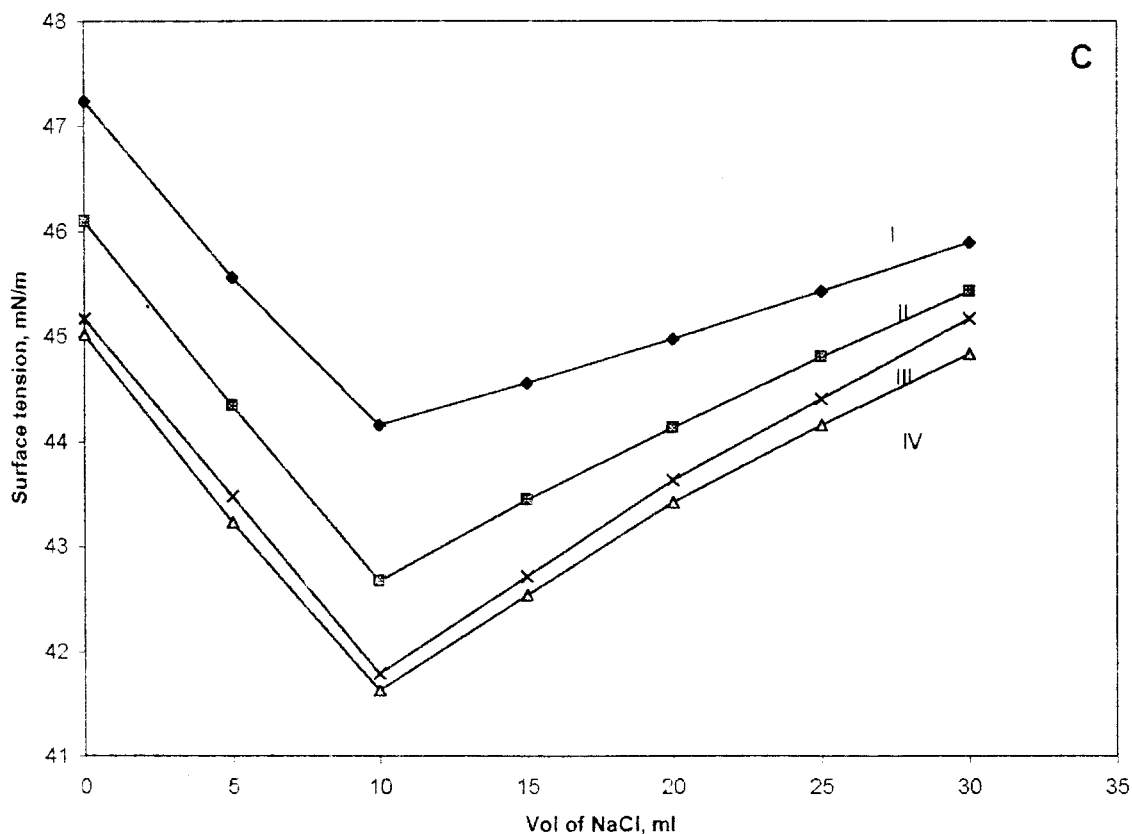


Figure 3 (Continued from the previous page)

is well reflected from the surface tension study (Fig. 3). Initially, the effect is due to the salting out effect of PVA, as addition of sodium chloride facilitates packing of PVA molecules because of its strong affinity of water. The increase in salt concentration disturbs the H-bonding between the PVA molecules and water. That is why the repulsion between the surface molecules of PVA is minimized and why it facilitates packing of PVA molecules; thus, the surface is enriched with the molecules. The surface tension value decreases and after completion of salting out the surface tension value increases because of the addition of NaCl surface-inactive agent; thus, there is an intersection between the two lines in Figure 3(A-C). The trend is quite similar irrespective of the concentration and molecular weight except the variation of 0.001% for M_w 14,000 [Fig. 3(A)]. In this case, the pattern is reversed. It seems that at this concentration, due to more dilution, the surface tension values increase with the addition of surface inactive agent, similar to the addition of NaCl in water. For low molecular weight PVA (M_w 14,000), the surface enrichment is enhanced in comparison to other molecular weights studied here. That is why the different trend is observed. With the addition of an appreciable quantity of 30% NaCl (W/V) (20 mL), the salting-out effect is reflected. In this case, there is a trend with the molecular weight of

the sample. For M_w 14,000 and 72,000, the intersection occurs at the added volume 15 mL NaCl, but for M_w 125,000, it occurs at a lower added volume of 10 mL. As the molecular weight is higher, there is more chance of packing with the low volume of NaCl to salting out. A similar effect was observed in the case of poly(ethyl glycol) (PEG).² This fact is more pronounced in the case of Na_2SO_4 . For salting out, the requirement of sodium sulfate is less because the affinity of water of sodium sulfate is more than sodium chloride and is according to the lyotropic or Hofmeister series of ion, where the effect is more due to the valency of the ion, $\text{SO}_4^{2-} > \text{Cl}^-$. Moreover, it has been also shown from the study of Leberman and Soper¹² that in the case of sodium sulfate, the equivalent pressure is more than sodium chloride. Both sodium and sulfate ions have significantly smaller partial molal volumes than water, which suggests that these ions have a substantial electrostrictive effect on water structures and so introduce disorder into the normal tetrahedral coordination of water molecules. Thus, the salting out effect of sodium sulfate is more than sodium chloride. The variation of surface tension with the concentration is rather the same as in the case of sodium chloride (Fig. 4). However, it can be also explained thermodynamically. The effect of salt type seems to be largely dependent on the anion, which

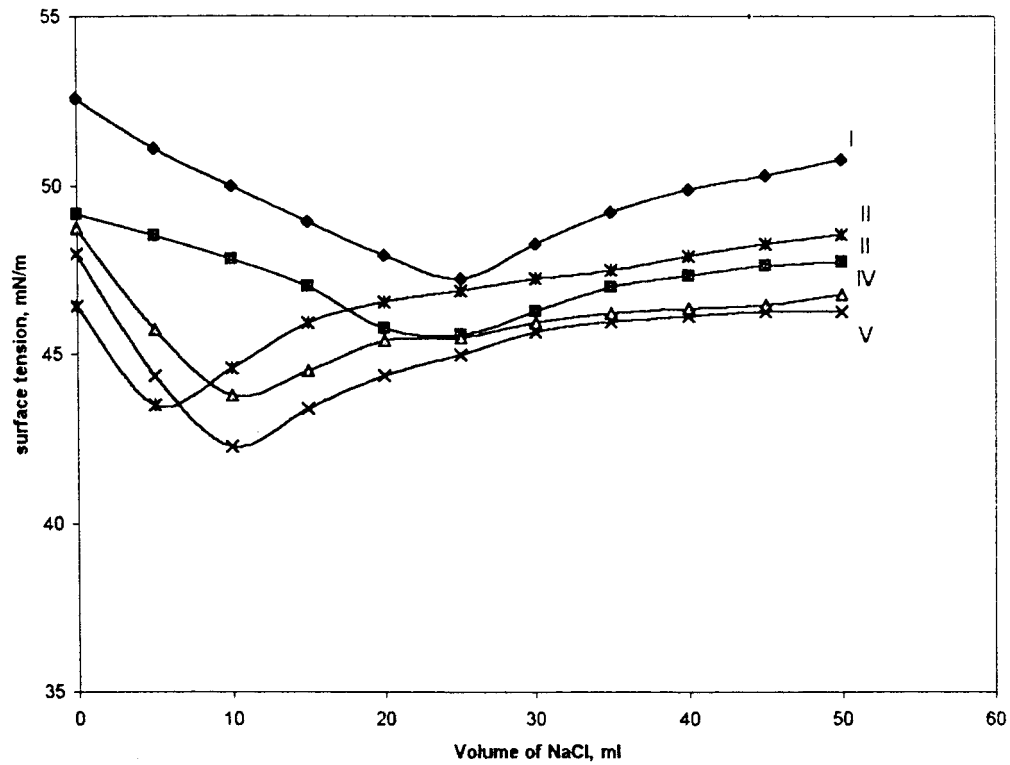


Figure 4 Effect of surface tension on addition of 30% NaCl solution to 1% PVA, M_w 72,000 (I) 15°C, (II) 25°C, (III) 35°C, (IV) 40°C, and (V) 45°C.

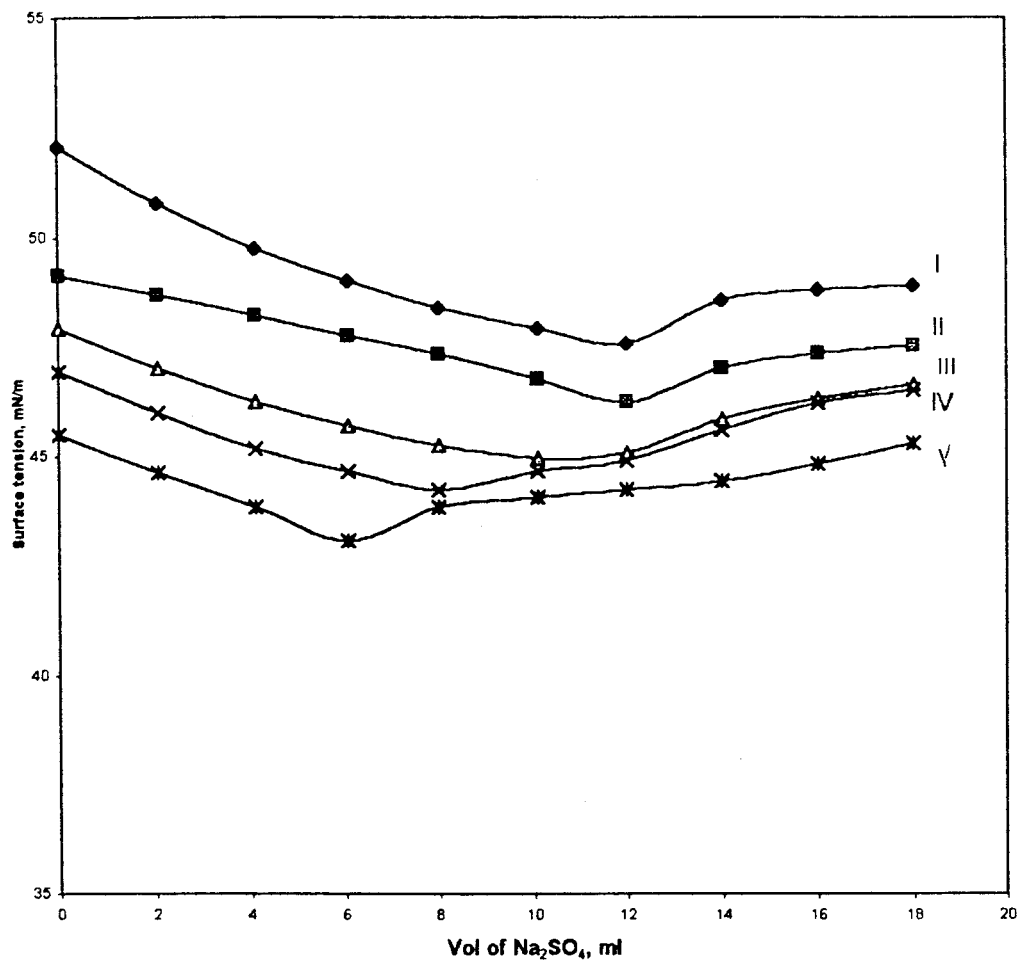


Figure 5 Effect of surface tension on addition of 10% Na₂SO₄ solution to 1% PVA, M_w 72,000 (I) 15°C, (II) 25°C, (III) 35°C, (IV) 40°C, and (V) 45°C.

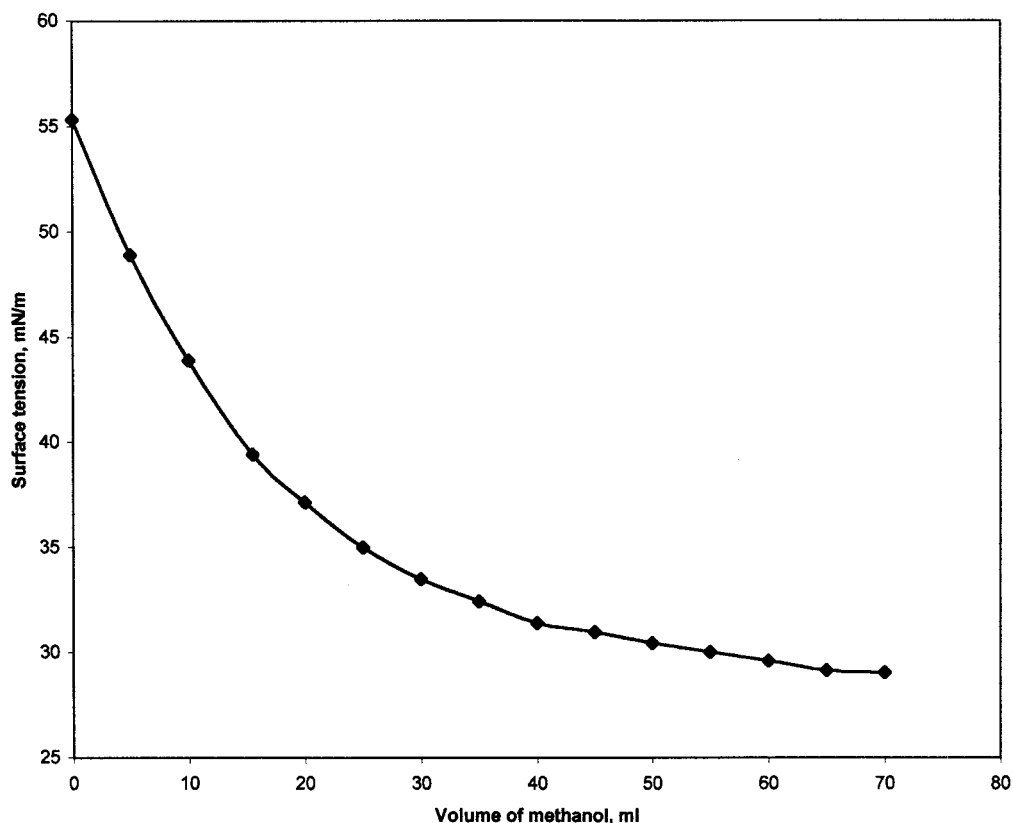


Figure 6 Variation of surface tension of PVA, M_w 72,000, on addition of methanol.

makes it the dominant contribution; this is reflected by its ΔG_{hyd} .¹⁵ The more negative the ΔG_{hyd} of the salt, the greater the salting-out effect of the salt.

When the temperature of the solution is increased, there is, in any case, a corresponding pressure increase. That is why the salting-out effect is more prominent in higher temperatures by adding a relatively small amount of sodium chloride. The temperature dependence regarding salting out was studied in the case of PVA (M_w 72,000). As the temperature is kept higher, it needs a low amount of NaCl to salt out. With an increase in temperature, the H-bonding between the PVA molecule and water disrupts and the packing of molecule enhances apart from the salting-out effect. The solution of Na_2SO_4 shows the same trend (similar to NaCl) in the temperature variation study (Fig. 5). In this case, the volume needed for salting out follows the order $45^\circ\text{C} > 40^\circ\text{C} > 35^\circ\text{C} > 25^\circ\text{C} = 15^\circ\text{C}$. There may be some minor volume difference or otherwise similarity because the H-bonding disruption effect is not very high in this temperature between 15 and 25°C .

However, we have carried out preliminary experiments on the addition of antichaotropic agents such as ammonium chloride, which shows salting in rather than salting out, as both ammonium and chloride ions have the partial molar volumes close to that of water

($\sim 18 \text{ cm}^3/\text{mol}$). These values do not change appreciably with concentration.^{16,17} These values affect the solubility of the polymer, which will be taken up in our future studies.

The addition of methanol affects the H-bond of the polymer and water molecules, the phase inversion of the process. The interaction parameter of methanol with water is higher than the polymeric interaction with water. Preliminary studies were carried out where addition of methanol lowers the surface tension. It shows no break point, as addition of methanol always lowers the surface tension (Fig. 6). Moreover, the nature of the curve is similar to the surface tension behavior of the methanolic addition of the water, except in the initial case, where the surface tension behavior is exceptionally high with respect to the surface tension of the polymeric solution.

CONCLUSION

The study of the surface tension of the polymer molecules is quite promising as it is the exception of other surface-active agents. The microstructure of the polymer molecules is dependent on the molecular weight and temperature. It has been also observed that water-mediated interactions are largely dependent on the addition of salts. The chaotropic

ions (viz. chloride and sulfate) have hindered the interchain H-bonding and results in salting out. The salting-out effect is temperature- as well as polymeric molecular weight dependent. The surface tension data are quite promising to establish the order of the Hofmeister series.

References

1. Huddleston, J. G.; Willauer, H. D.; Griffin, S. T.; Rogers, R. D. *Ind Eng Chem Res* 1999, 38, 2523.
2. Willauer, H. D.; Huddleston, J. G.; Rogers, R. D. *Ind Eng Chem Res* 2002, 41, 1892.
3. Mark, H. F.; Gaylord, N. G.; Bikales, N. M. *Encyclopedia of Polymer Science and Technology*; Wiley Interscience: New York, 1971, Vol. 14.
4. Ananthapadmanabhan, K. S.; Goddard, E. D. *J Colloid Interface Sci* 1986, 113, 294.
5. Willauer, H. D.; Huddleston, J. G.; Griffin, S. T.; Rogers, R. T. *Sep Sci Technol* 1999, 34 (6&7), 1069.
6. Kalra, A.; Tugcu, N.; Cramer, S. M.; Garde, S. *J Phys Chem B* 2001, 105, 6380.
7. Hummer, G.; Garde, S.; Garcia, A. E.; Paulaities, M. E.; Pratt, L. R. *J Phys Chem B* 1998, 102, 10469.
8. Lundqvist, H.; Eliasson, A. C.; Olofsson, G. *Carbohydr Polym* 2002, 49 (1), 43.
9. Djuve, J.; Pugh, R. J.; Sjoblom, J. *Colloids Surf, A* 2001, 186 (3), 189.
10. Jones, M. N. *J Colloid Interface Sci* 1967, 23, 36.
11. Schwartz, A. M.; Perry, J. W. *Surface Active Agents*, 3rd ed.; Interscience Publishers: New York, 1957; Vol. 1.
12. Leberman, R.; Soper, A. K. *Nature* 1995, 378, 364.
13. Postorino, P.; Tromp, R. H.; Ricci, M. A.; Soper, A. K.; Nielson, G. W. *Nature* 1993, 366, 668.
14. Ananthapadmanabhan, K. P.; Goddard, E. D. *Langmuir* 1987, 3, 25.
15. Rogers, R. D.; Bond, A. H.; Bauer, C. B.; Zhang, J.; Griffin, S. T. *J Chromatog B* 1996, 680, 221.
16. Millero, F. J. *Chem Rev* 1971, 71, 147.
17. *Hand Book of Chemistry and Physics*, 55th ed.; CRC: Cleveland, 1976; D194–D236.