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Surface and interfacial activities of hydrophobically modified poly(vinyl alcohol) (PVA)

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In the present study, the air–liquid surface and liquid–liquid interfacial activities of hydrophobically modified poly(vinyl alcohol) (PVA) solutions were investigated to determine the effects of NaCl concentration, polymer concentration, time, polymer molecular weight, polymer modification and the average length of the hydrophobic side groups. The hydrophobically modified PVA exhibit high air–liquid surface and liquid–liquid interfacial activities which increase with increasing NaCl concentration, polymer concentration, molecular weight and average length of the hydrophobic side groups. The observed strong dependence of surface and interfacial activities on salt concentration for this non-polyelectrolyte polymer is explained in terms of the reduced polymer solubility or salting out with increasing salinity.

(Keywords: poly(vinyl alcohol); surface tension; interfacial tension; associating polymers)

INTRODUCTION

Hydrophobically modified poly(vinyl alcohol) (PVA) has the potential of high surface and interfacial activities as a result of its amphiphilic structure, i.e. it consists of hydrophilic groups (hydroxyl and urethane groups) and hydrophobic moieties (long-chain fatty acid groups). Amphiphilic polymers form monomolecular or polymolecular micelles in aqueous solutions[1–10], and have enhanced ability to adsorp at an interface. This can lead to a sharp reduction in surface and interfacial tensions of the polymer solution. Such polymers are also expected to exhibit enhanced viscosification ability as a result of intermolecular hydrophobic interaction between the hydrophobic groups in the structure, thus leading to the formation of polymolecular associations and hence to structures with large hydrodynamic volume.

In view of this expected behaviour of amphiphilic polymers, we became interested in their preparation and subsequent investigation of their aqueous solution properties. Chemical modification of a pre-formed reactive polymer was used in this work to modify PVA. The polymer is chemically modified by grafting urethane and alkyl groups to its main chain. The detailed preparation and viscosity behaviour of the polymer have been reported in a previous publication[8]; this paper presents the surface and interfacial tension behaviour. The surface and interfacial tension behaviour of the hydrophobically modified PVA was investigated with respect to the NaCl concentration, polymer concentration, time, polymer molecular weight and the effect of the polymer modification. The hydrophobically modified PVA obtained in this work exhibits high surface and interfacial activities which increase with increasing polymer and NaCl concentration and molecular weight.

EXPERIMENTAL

Materials and polymer preparation

Preparation of materials and the polymer has been discussed previously[8,11]. The degree of urethanization for these polymers is estimated at around 15 mol% of the vinyl alcohol (VA) units[8,11]. Basically, the modified polymers were prepared by reacting different combinations and ratios of three acid chlorides with partly urethanized PVA having a degree of polymerization of 1600 or 2000. Partly urethanized PVA was prepared by treating PVA with urea in distilled dimethyl formamide (DMF) at ~150°C. Two polymers with different hydrophobic contents were prepared. Polymer I contained 0.5 mol% C22 (docosanoic acid chloride), 0.5 mol% C18 (stearic acid chloride) and 1.0 mol% C10 (decanoic acid chloride) as hydrophobic content, and polymer II contained 2.0 mol% C18 (stearic acid chloride) and 1.0 mol% C10 (decanoic acid chloride) as hydrophobic content. These two polymers were chosen for detailed study from the 18 modified polymer candidates prepared in the earlier work because polymer I exhibited the highest surface activity and polymer II gave the highest solution viscosity.

An example of a modification reaction is as follows: urethanized PVA (4 g), having a degree of polymerization of 1600 and a molecular weight of 72 000, was mixed with distilled DMF (40 ml), heated to 140°C and maintained at this temperature until a clear homogeneous solution was obtained. Next, the three

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combinations of the acid chlorides—i.e. 0.148 g C22 (0.5 mol% docosanoic acid chloride substitution), 0.125 g C18 (0.5 mol% stearic acid chloride substitution) and 0.157 g C10 (1.0 mol% decanoic acid chloride substitution), which had previously been mixed in a small test tube—was introduced dropwise into the reaction mixture maintained at 140°C, and stirred vigorously. The reaction was carried out under N_2 gas to prevent degradation of free radicals by O_2. After 2 min reaction time, the resulting polymer was precipitated into methanol, purified twice in excess methanol, and then dried *in vacuo* at 70°C. The reaction scheme and structure of the hydrophobically modified PVA are given in *Figure 1*.

Measurements

To study the surface and interfacial activities of the hydrophobically modified PVA, stock solutions were prepared at least 24 h before use. Final solutions of the desired composition were obtained by dilution of the appropriate stock solution with water and, if necessary, addition of an appropriate amount of solid NaCl. Most of the dissolution processes took 2–3 days.

The air–liquid surface tensions of the modified polymer solutions were determined using the plate method (Processor Tensiometer K12, Kruss). All measurements for different polymer concentrations were performed at 30°C. The surface tension was also measured for a polymer concentration of 0.5 wt% with different NaCl concentrations ranging from 0.1 to 7.0 wt%. The n-decane–water interfacial tensions (*IFT*) of the modified PVA solutions were determined using the ring method (Processor Tensiometer K12, Kruss). The *IFT* of the aqueous solution/n-decane was measured for two polymer concentrations, 0.5 and 2.0 wt%, at different NaCl concentrations ranging from 0 to 7.0 wt%, and all the measurements were performed at 25°C. Attempts were also made to measure the *IFT* for higher polymer concentrations, such as 5.0 wt% polymer concentration, with different NaCl concentrations. Unfortunately, it was difficult to get reliable results due to the very high viscosity of the polymer solution, but the *IFT* decreases with increasing polymer concentration.

RESULTS AND DISCUSSION

Surface tension behaviour

The air–liquid surface and liquid–liquid interfacial tensions of polymer I (with 0.5 mol% C22, 0.5 mol% C18 and 1.0 mol% C10 degree of substitution) and polymer II (with 2.0 mol% C18 and 1.0 mol% C10 degree of substitution) were studied under various conditions of salinity, polymer concentration, polymer modification, time in solution and polymer molecular weight.

In addition, the hydrophobic–lyophobic balance (*HLB*) numbers for these polymers were calculated based on the repeat unit per hydrophobic side chain. These were obtained by calculating the *HLB* number for each of the hydrophobic side-chain groups attached to the polymer main chain and determining the average from the three. The group numbers for the hydrophilic and hydrophobic groups in the polymers were assumed to be the same as the ones obtained for surfactants[12]. These numbers were used to calculate the *HLB* number of the polymers. For polymer I, an *HLB* number of 64.2 was obtained, while that for polymer II was 64.0.

These numbers are very high when compared with previous values obtained for surfactants[12]. The numbers

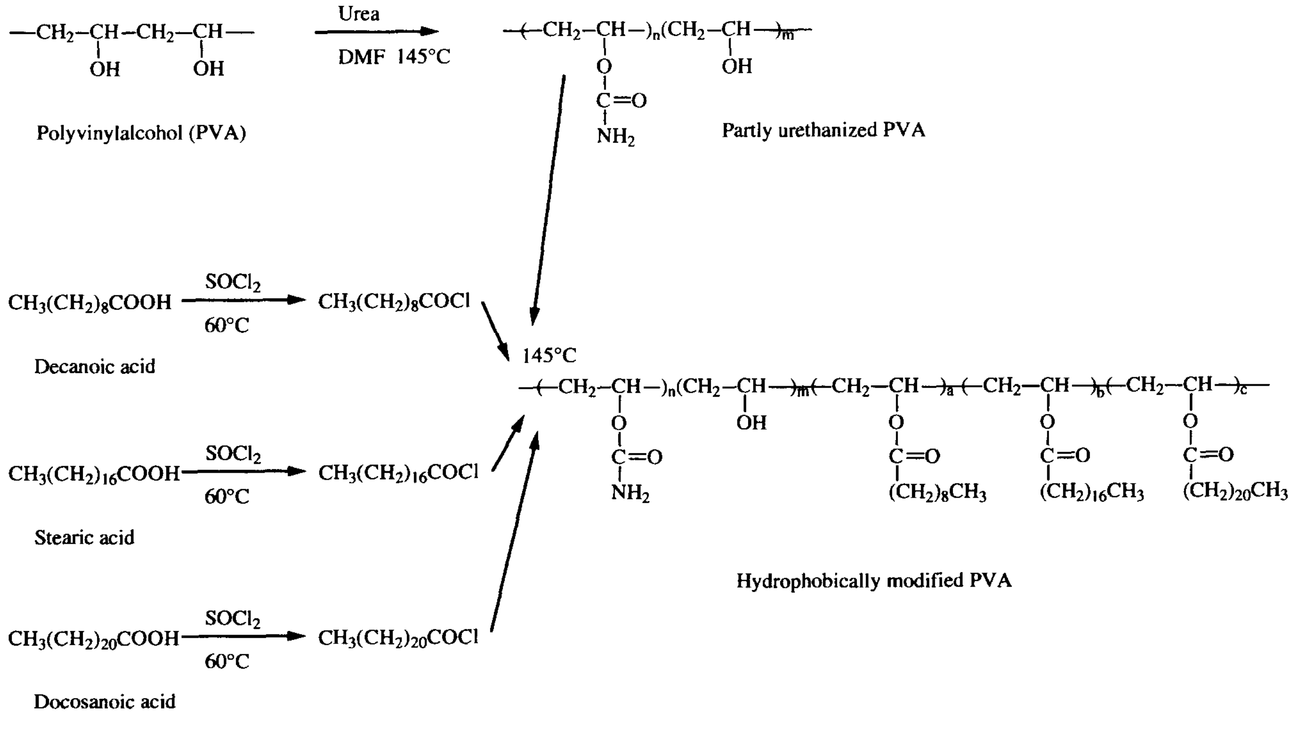

Figure 1 Reaction scheme and molecular structure of hydrophobically modified PVA

would be expected to increase even further if the contribution from urethane groups (one of the hydrophilic groups in the polymer main chain) was considered in the calculation. This was not considered in our calculation because, to our knowledge, the group number for this hydrophilic group is not available in the literature. These high *HLB* numbers can be attributed to the assumption that all the groups in the polymers, most especially the OH group, make the same hydrophilic contribution (i.e. have the same group number) as in surfactants[12], which is manifestly incorrect.

Figures 2–5 depict the effects of polymer modification, polymer concentration, NaCl concentration, time and polymer molecular weight on the surface tension of polymer I which has hydrophobic substitution of 0.5 mol% C22, 0.5 mol% C18 and 1.0 mol% C10. As shown in *Figure 2*, this hydrophobically modified PVA exhibits a higher surface activity than the original and the urethanized PVA. The surface tension of the hydrophobic polymer is observed to be lower than that of the unmodified PVA and also to decrease with increasing polymer concentration. The incorporation of the hydrophobic groups is the primary factor causing this increase in surface activity. The presence of the hydrophobic groups makes it more favourable for the polymer to adsorb on the interface, where these hydrophobic groups can extend in the air or hydrocarbon phase. Furthermore, urethanized PVA is also observed to exhibit more surface activity than the original PVA, as can be seen from the lower surface tension of the former compared with the latter. However,

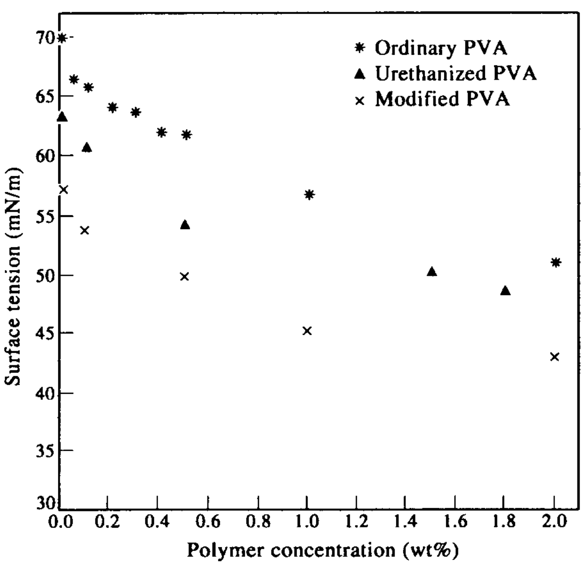

Figure 2 Surface tension *versus* polymer concentration for modified (polymer I), urethanized and original PVA with molecular weight of 72 000 at 30°C

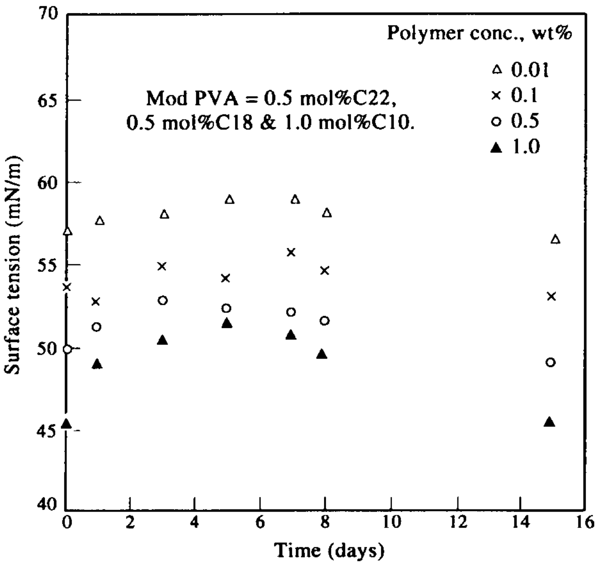

Figure 3 Variations of surface tension–time relationship with polymer concentration for modified PVA (polymer I) of molecular weight 72 000 at 30°C

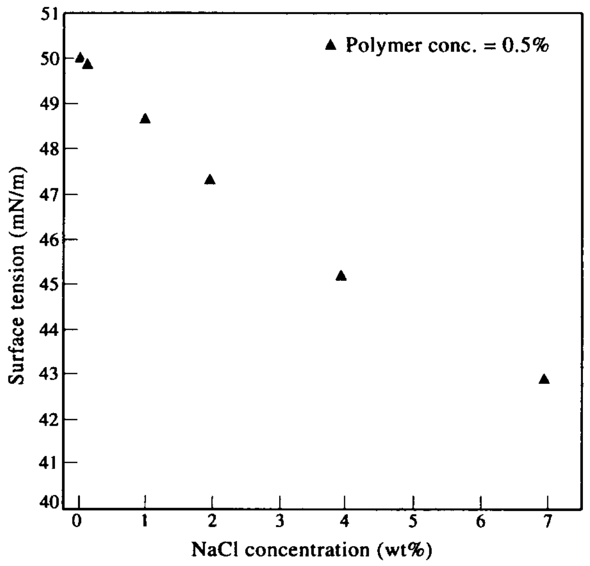

Figure 4 Effect of NaCl on the surface tension of modified PVA (polymer I) with molecular weight of 72 000 at 30°C

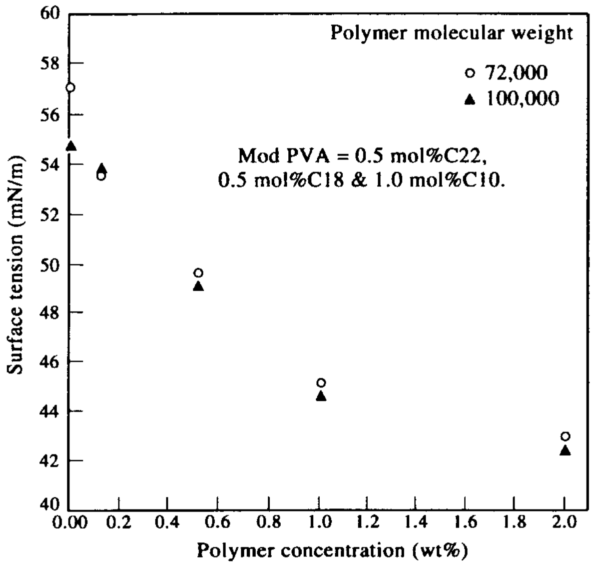

Figure 5 Effect of polymer molecular weight on the surface tension–polymer concentration relationship for modified PVA (polymer I) at 30°C

the surface tension of the modified PVA is much lower than those of urethanized and original PVA.

As shown in *Figure 5*, a sharp decrease in surface tension is observed with increasing polymer concentration for molecular weights of 72 000 and 100 000. No critical micelle concentration (*CMC*) or break point resembling a *CMC* is observed for this polymer, in contrast to previous observations for an oligomeric polymer[7,13]. The surface tension decreases throughout the range of polymer concentrations considered. The decrease in the surface tension is due to the increased adsorption of the available polymer molecules at the air–aqueous solution interface as the polymer concentration increases.

The surface tension of the hydrophobically modified polymer is also observed to be time-dependent. The time dependence of surface tension for the polymer of molecular weight of 72 000 is displayed in *Figure 3*. A maximum in surface tension is observed between 6 and 8 days of measurement, after which a decrease in surface tension is observed from 8 up to 15 days. This behaviour is observed for all the polymer concentrations considered at 30°C. The decrease in surface tension of the modified polymer with time can be attributed to the slow reorientation of the bulky polymer molecules at the air–aqueous solution surface. Extensive equilibration times are required due to slow diffusion and conformational changes of the polymers[14]. Similar trends have also been observed by Okubo[15] and Ishimuro and Ueberreiter[16].

Furthermore, it is observed that adding NaCl to the polymer solution increases its surface activity. The surface tension is observed to decrease drastically with increasing NaCl concentration up to 7.0 wt%, beyond which a precipitate was formed. The surface tension is depicted in *Figure 4* for the modified polymer of molecular weight of 72 000 and concentration of 0.5 wt%. This behaviour of the polymer with NaCl is an interesting feature because the polymer may be suited for applications where high salinities are encountered, such as in enhanced oil recovery processes. The behaviour can be attributed to the increased adsorption of polymer molecules at the air–aqueous solution interface as the NaCl is added. In essence, NaCl is making the aqueous phase less favourable for the polymer molecules, causing more molecules to go to the interface and consequently reducing the surface tension. Furthermore, since the polymer under investigation is a non-polyelectrolyte polymer, the reduction in surface tension with NaCl could not have been due to the neutralization of changes on the polymer molecules by the added NaCl. This behaviour is therefore unusual because non-polyelectrolyte polymers usually exhibit little change in surface activity with salt. Apparently, the added salt makes the water less hospitable to the hydrophilic moieties of the polymer, thus promoting more polymer adsorption at the surface. This also explains the polymer precipitation at high salt concentration.

Figure 5 shows the effect of molecular weight on the surface tension of polymer I. The hydrophobically modified PVA of molecular weight of 100 000 is observed to have a slightly higher surface activity than that of molecular weight 72 000. This behaviour is observed for all the polymer concentrations considered at 30°C. The slight decrease in surface tension with increasing polymer molecular weight is consistent with models that predict that the surface tension decreases with the natural log of the molecular weight[17].

Figure 6 shows the effect of polymer concentration, modification and NaCl salt on the surface tension of polymer II with hydrophobic groups combination of 2.0 mol% C18 and 1.0 mol% C10. As mentioned earlier, polymer I exhibits a greater surface activity than polymer II. As shown in *Figure 6*, the surface tension of the former is lower and decreases more drastically with increasing polymer concentration than that of the latter. This behaviour can be attributed to the presence of the long C22 hydrophobic groups in polymer I. The surface tension of polymer II also decreases with increasing polymer concentration and NaCl concentration, as observed for polymer I.

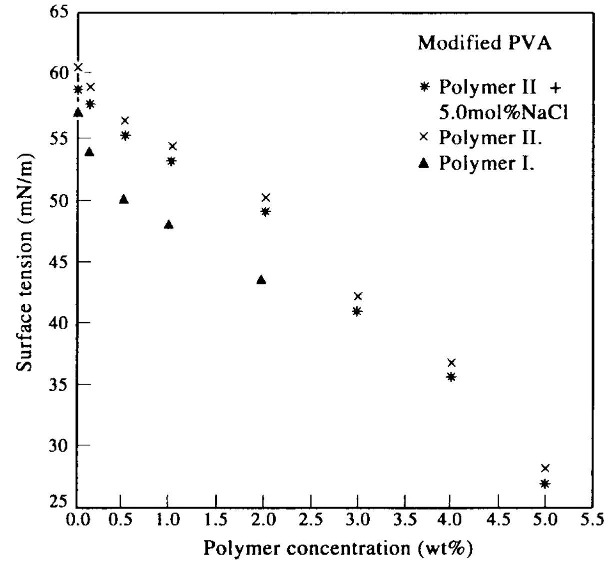

Figure 6 Effects of polymer concentration, modification and NaCl on the surface tension of modified PVA (polymer II) with molecular weight of 72 000 at 30°C

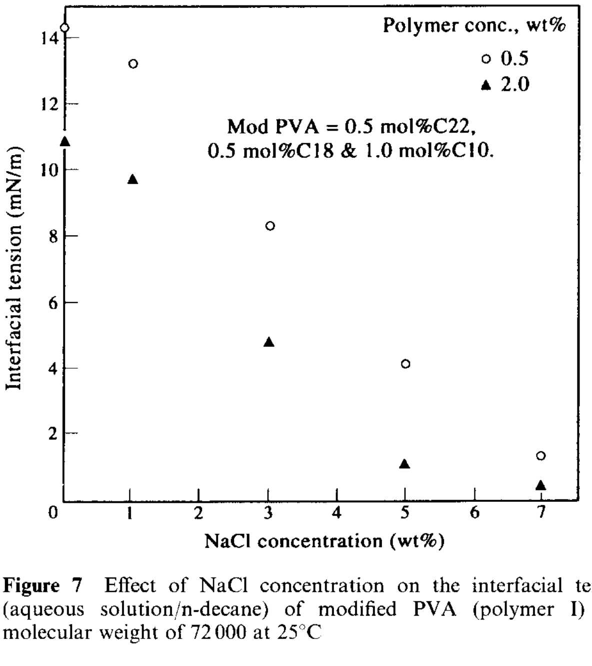

Figure 7 Effect of NaCl concentration on the interfacial tension (aqueous solution/n-decane) of modified PVA (polymer I) with molecular weight of 72 000 at 25°C

Interfacial tension behaviour

Figures 7–9 depict the effects of polymer concentration, NaCl concentration, polymer molecular weight and the effect of modification on the *IFT* of polymer I. As expected, the *IFT* decreases as the polymer concentration increases, as shown in *Figures 7* and *8*. The decrease in the *IFT* is due to the increased adsorption of the available polymer molecules at the aqueous solution—n-decane interface as the polymer concentration increases. This trend is observed for the two molecular weights of 72 000 and 100 000 and for all the different polymer/NaCl solution combinations considered, and is typical of surface-active molecules.

The decrease in *IFT* with increasing NaCl concentration is similar to what has been observed earlier for the surface tension. *IFT* decreases with increasing NaCl concentration for both polymers (molecular weight of 72 000 and 100 000), as depicted in *Figures 7* and *8*. However, this behaviour is unusual for non-ionic polymers like the ones under consideration. Non-polyelectrolyte polymers usually exhibit little change in surface activity with salt. In fact, it has been reported that, in contrast to the polyelectrolyte polymers, the surface activity of zwitterionic polysoaps is reduced by adding salt owing to their anti-polyelectrolyte character[14]. However, the hydrophobically modified PVA under investigation exhibits a contrasting behaviour to typical non-ionic polymers.

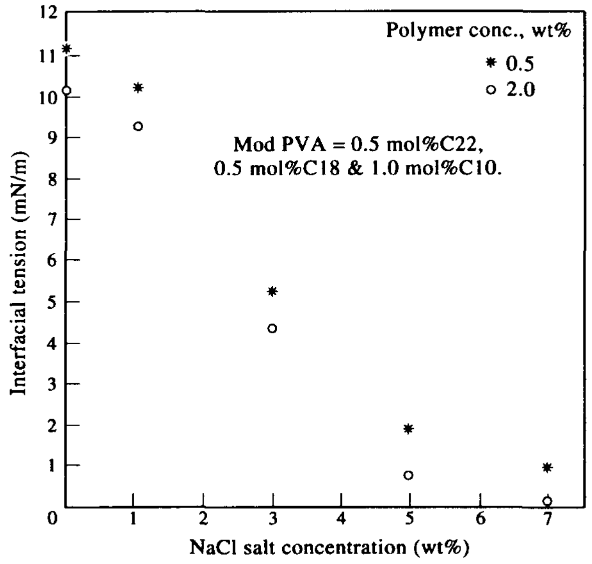

Figure 8 Effect of NaCl concentration on the interfacial tension (aqueous solution/n-decane) of modified PVA (polymer I) with molecular weight of 100 000 at 25°C

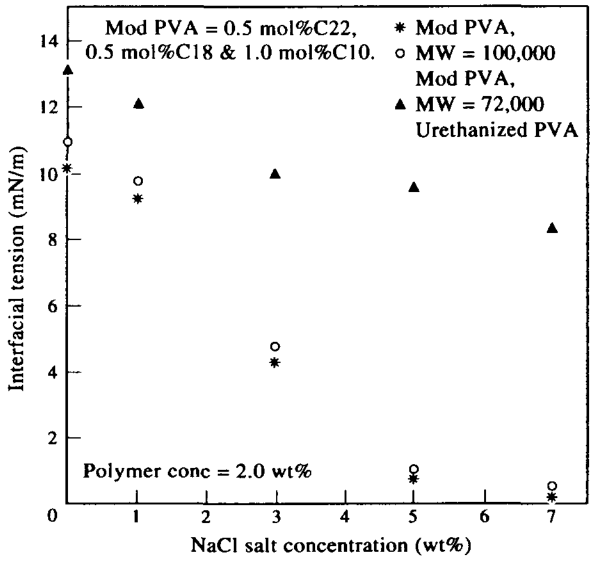

Figure 9 Effects of NaCl concentration, molecular weight and modification on the interfacial tension (aqueous solution/n-decane) of modified PVA (polymer I) at 25°C

Figure 9 shows the effects of NaCl, molecular weight and modification on the *IFT* of polymer I. As observed earlier, the *IFT* decreases with increasing NaCl concentration for urethanized PVA and the two molecular weights of 72 000 and 100 000. The modified PVA is observed to exhibit higher interfacial activity than the urethanized PVA for the same polymer concentration of 2.0 wt%, as discussed earlier. As observed earlier for the surface tension, polymer I of molecular weight of 100 000, is observed to have a slightly lower *IFT* than modified PVA with molecular weight of 72 000 at the same polymer concentration of 2.0 wt%.

CONCLUSION

As a result of their hydrophobic structure, the associating polymers considered in this work exhibit good surface and interfacial activities. No *CMC* or break point resembling a *CMC* is observed for the hydrophobically modified PVA. Increasing the concentration of NaCl in the polymer solution decreases its surface and interfacial tensions, an unusual behaviour for non-polyelectrolyte polymers. The polymer also exhibits higher surface and interfacial activities for higher molecular weight than for lower molecular weight. Increasing the polymer concentration also leads to the increase in the surface and interfacial activities of the modified polymers.

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