Properties of Hydroxypropyl Methylcellulose–Polyvinyl Alcohol Water Systems, Dispersants in Vinyl Chloride Suspension Polymerization

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SYNOPSIS

Aqueous solutions of partly hydrolyzed polyvinyl acetate (polyvinyl alcohol, PVA) and hydroxypropyl methylcellulose (HPMC) are used together as dispersants in vinyl chloride suspension polymerization. Surface tension, viscosity, and cloud point (CP) of diluted PVA and HPMC solutions at room temperature, viscosity of concentrated solutions as a function of temperature, and incipient gelation temperatures (IGT) were determined. Viscosity measurements show synergism of binary polymer mixtures. The synergetic effect diminishes with rise of temperature. IGT of PVA–HPMC solutions do not differ remarkably from those of solutions containing only HPMC and are much higher than the corresponding CP. At definite relative concentrations of HPMC and PVA, separation of the mixtures into two immiscible phases occurs. Each phase contains both polymers, but in the denser and more concentrated phase (lower layer), PVA is the prevailing component. The mutual influence of the two polymers causes changes in solute–solvent interaction, that is, dehydration of the polymers' molecules. It is assumed that in the processes occurring in the system, preferential molecules of definite structure take part. The merits of a system using both polymers as dispersants in the vinyl chloride polymerization are discussed in the light of ascertained data. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The physical properties of suspension polymers depend primarily on the conditions of agitation during the polymerization and on the dispersing agents used in the process. These factors regulate the degree of coalescence of monomer droplets and the morphology of polymer particles. The nature of the dispersing agents determines such physical properties of the polymers as average particle size, particle size distribution, porosity, bulk density, and transparency.[1] In the case of vinyl chloride polymerization, the dispersing agents affect also the chemical stability of the polymer, because the former can react with PVC and, in such a way, remain in the particles of the final polymer.[2,3] Formation of agglomerates on the reactor surface during the polymerization, which is very undesirable, is diminished by the use of appropriate dispersing systems.

In vinyl chloride suspension polymerization the dispersants most often used are water-soluble polymers: polyvinyl alcohol (PVA), that is, polyvinyl acetate hydrolyzed to various degrees, and cellulose ethers, hydroxypropyl methylcellulose (HPMC), that is, cellulose, substituted by methyl and 2-hydroxypropyl groups to various degrees. These polymers lower the interfacial tension between the water and monomer phases and so help to stabilize the initial dispersion of monomer droplets in water and to form polymer particles of desirable structure.[1,4] Although the level of water-soluble polymers used in suspension polymerization is very low and they give a relatively small increase in aqueous-phase viscosity, changes in viscosity are enough to alter the structure of PVC particles. It was shown by Cebullada et al.[5] that increase of aqueous-phase viscosity in the narrow range of 0.545–0.992 cS (at 60°C) caused by using HPMC of various polymerization and substitution degrees, to a great extent alters the average size and morphology of PVC particles. Hence, the efficiency of the dispersants depends not only on the interfacial tension and vis-

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cosity of the aqueous-phase but also on the chemical structure of the dispersant molecules. The latter determines the physical nature of the adsorbed films and also of the semicellular membranes or skins formed on the surface of the dispersed liquid and of the polymer particles. These adsorbed films and membranes or skins act as mechanical barriers between the phases and so regulate the intensity of coalescence in the system and, thus, the structure of the final PVC particles.[6,7] The physical state of the dispersants is also of importance. From the publication of Shiraishi and Toyoshima,[2] it may be drawn that PVA dispersing solutions with lower cloud point (CP) are more efficient. According to Sarkar,[8] in suspension polymerization the gelation of the adsorbed cellulose ethers on the monomer droplets provide stability of the system. Obviously, the final properties of the PVC particles are determined to a great extent by the hydrophylic–hydrophobic balance existing in the dispersing solution.

The use of only one dispersant is often not enough to provide the necessary dispersing power of the aqueous phase during the polymerization of vinyl chloride. Therefore, such dispersants as PVA and HPMC are used together with some additives.[4] Many manufacturers are using dispersing systems containing both PVA and HPMC. According to the patent literature, during polymerization in the presence of PVA–HPMC systems the overall concentration of both polymers in water may be less than that of polymerization in the presence of individual dispersants. It is also known that the PVC particles' properties greatly depend on the ratio between the components of the dispersing system; and the ability of the system is not an additive function of the ones related to PVA and HPMC alone.

The properties of aqueous solutions containing both PVA and cellulose ethers are not described in the literature. However, it is known that aqueous highly hydrolyzed PVA may be not compatible with cellulose ethers other than HPMC.[9]

In this work properties of PVA–HPMC aqueous solutions are studied. We investigated the viscosity, surface tension, and IR spectra of such solutions, and also the compatibility of the two polymers in water.

EXPERIMENTAL

Materials

Two grades of HPMC from Dow Chemical were used as received. Some features are summarized below:

Product Designation	Viscos- ity[a] (cP)	Meth- oxyl Groups[b] (%)	2-Hydroxy- propoxyl Groups[b] (%)
Type 1			
(K100-LV)	77	22.1	9.1
Type 2 (F50)	50	28.7	5.3

[a] 2% aqueous solution, 25°C.

[b] Determined according to ASTM norm D 2363-79.

The PVA (Alcotex 72.5 from Revertex Ltd.) was also used as received. Its properties: viscosity (4% aqueous solution at 25°C) 6.0 cP, vinyl acetate units 27.5 mol %.

Procedures

Surface tension of HPMC and PVA solutions was measured with a DuNouy type tensiometer.

Viscosities of diluted polymer solutions were measured with an Ubbelohde type capillary viscometer.

The dependence of the viscosity of concentrated solutions on the temperature was obtained by using a Haake Rotovisco viscometer Model RV-2 (Haake, Inc., Saddlenbrook, NY). The incipient gelation temperatures (IGT) of the polymer solutions were obtained according to the method of Sarkar[8] by measuring the viscosity of the solution (at a constant rate of shear) as a function of temperature while raising it 0.5°C/min. The temperature at which the viscosity is minimum is called IGT.[8] The IGT values were measured to an approximation of ±1°C.

The method of Zdanovski[10] was used for calculation of the expected viscosity values for solutions of two polymers. This method is based on the assumption that fluidity (the inverse of viscosity) is proportional to the relative free volume of the dissolved substance. If, after mixing of two solutions the character of macromolecules' solvation and binding that took place in each of them before mixing was not changed, and the density of the initial solutions was practically the same, the viscosity could be calculated using the following equation:

$$\eta = \frac{100}{X_1/\eta_1 + X_2/\eta_2} \qquad (1)$$

where X_1, X_2 are volume percent of each solution

Table I   Surface Tension of Aqueous Solutions of PVA and HPMC (Type 1) at 26°C

PVA (%)	HPMC (%)	Surface Tension (dynes·cm^{-1})	PVA (%)	HPMC (%)	Surface Tension (dynes·cm^{-1})
0.0015	—	49	—	0.01	53
0.005	—	46	—	0.1	52
0.01	—	46	0.0015	0.0085	51
0.1	—	46	0.005	0.005	46
—	0.005	52	0.05	0.05	45

in the mixture, and η_1, η_2 are viscosities of the initial solutions.

To determine the CP of a polymer solution the latter (100 mL) was heated in a glass beaker using a magnetic stirrer hot plate. The solution temperature was raised at 2°C/min. The temperature at which the onset of turbidity was visually observed was the CP. The reproducibility of the CP determinations was within ±1°C.

In order to evaluate heterogenity of the systems, fixed quantities of PVA, HPMC, and water were heated to 60–65°C with mixing in a cylindrical glass beaker, then slowly cooled without mixing and left to stand at 26°C for 2–72 h until the solutions were completely transparent. If two layers were formed, the height of each of them was measured. In some cases, especially at high concentrations of the polymers, the prepared two-phase mixtures were allowed to stand at 26°C in a separating funnel. The transparent layers were separated and weighed. Using these data the percent part of the lower layer was calculated.

In order to determine the content of polymers in aqueous solutions, weighed samples of them in a tared dish were heated at 95–100°C until most of the water evaporated and then dried for 2 h in an oven at 105°C. The remaining residue had the same color as the initial polymers. It was weighed and its percent calculated.

Determination of the content of PVA vinyl acetate units in aqueous solutions of PVA and HPMC was performed (as recommended by the PVA producer) by hydrolysis of weighed samples in the presence of excess sodium hydroxide and methanol. Because of the presence of HPMC in the mixture, addition of a few drops of silicone antifoaming agent was necessary.

FTIR spectra of aqueous solutions of polymers were taken on an 5ZDX Nicolet FTIR spectrophotometer with accessory of a Squarecol Liquid ATR (attenuated total reflectance) Model 1180 from Specac Ltd.

RESULTS AND DISCUSSION

Properties Close to Room Temperature

The effect of dispersants on surface tension was investigated in diluted solutions. As seen from Table I the HPMC as surfactant is less active than PVA, and the surface tension of solutions containing both polymers is determined by that of the more active surfactant. Analogous results were obtained with more concentrated solutions of PVA and HPMC, and by replacing HPMC of Type 1 by Type 2.

Viscometric investigations began with determination of viscosity of homogeneous HPMC (Type 1)–PVA water systems at a temperature (25°C) lower than their CP (see ff.). The viscosity values found for solutions containing 0.1% of both HPMC and PVA, to some extent, exceeded the calculated one (Table II). The deviations of the experimental data from the expected, based on the assumption of the additivity of the fluidity values for the initial solutions, increase with growth of the concentrations

Table II   Viscosities of Homogeneous HPMC (Type 1)–PVA Solutions at 25°C

| HPMC (%)	PVA (%)	Viscosity (cP) Calculated According to eq. (1)	Viscosity (cP) Found
0.1	—	—	1.192
0.085	0.015	1.138	1.161
0.07	0.03	1.088	1.121
0.05	0.05	1.029	1.040
0.03	0.07	0.992	1.009
0.015	0.085	0.939	0.949
—	0.1	—	0.905
0.3	—	—	2.066
0.15	0.15	1.321	1.450
—	0.3	—	0.971

of dissolved polymers (see experiments with 0.3% concentration of the polymers in water). The increased viscosity of HPMC–PVA solutions shows that both polymers dissolved in water influence each other.

Mixing of HPMC and PVA solutions leads to decrease of the CP. Therefore, a 0.1% solution of HPMC (Type 1) that did not grow turbid up to 70–75°C was added to an equal amount of 0.1% solution of PVA with a CP of 32–34°C. A solution with a CP of 30–32°C was obtained. At temperatures higher than the CP this solution was more turbid than the initial one containing only PVA. Solutions containing 1% and more of each PVA and HPMC (Type 2) were turbid also after cooling to 8°C (CP of solutions of the latter HPMC were about 55–60°C). Hence, HPMC acts formally as a nonsolvent in regard to PVA dissolved in water. The heterogenization of the ternary HPMC–PVA water systems may be explained by dehydration of the solutes. Evidently, when present together, HPMC and PVA

molecules are more hydrophobic and less hydrated than self-associated ones.

Viscometric Behavior in Dependence on Temperature

The dependence of viscosity of the HPMC–PVA aqueous solutions on temperature is quite complex. Typical curves showing the dependences found are given in Figure 1. Viscometric behavior in Figure 1(A) is similar to that by Sarkar.[8] Tables III and IV and Figure 2 include all the results found on heating of HPMC (Type 1)–PVA water systems. As is seen, although PVA gives low-viscosity solutions (viscosity of 2% solution at 55°C is less than 2 cP), its addition leads to a considerable viscosity increase of HPMC solutions practically in the entire range of temperatures used. At constant HPMC content, on increasing of PVA addition from 25% up to 200% causes the viscosity to rise systematically (Table III). Viscosities of solutions of constant total
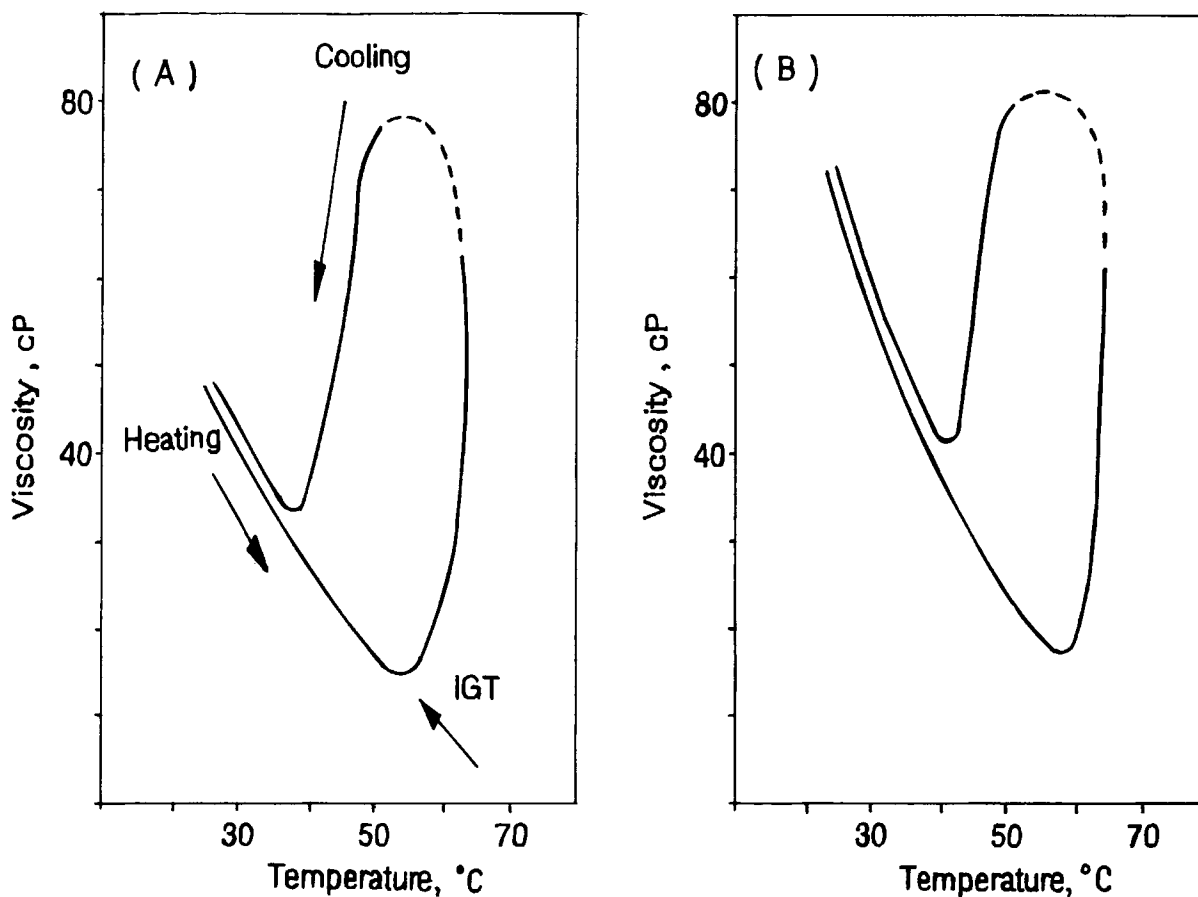
Figure 1 Gelation of 2% aqueous solutions of HPMC (Type 2) on heating in (A) absence and (B) in the presence of 1% PVA.

Table III   Change of Viscosity (cP) for 2% Aqueous Solutions of HPMC (Type 1) in the Presence of Different Amounts of PVA

Temperature (°C)	PVA (%)				
	0	0.5	1.0	2.0	4.0
25	75	88	132	233	450
35	52	64	92	156	290
45	37	44	62	101	165
55	30	33	42	66	70
65	22	23	31	44	58
70	18	16	19	> 60	> 60
73	> 30	> 30	> 30		

Rate of shear = 32 sec^{-1}.

concentration of both dispersants at different ratios between them are shown in Figure 2. As seen from the inflexion of the curve and also from data in Table III the synergism of HPMC and PVA shows itself (at 55°C) most strongly when the contents of PVA and HPMC approach each other. Apparently, the greatest strengthening of hydrophobe–hydrophobe interaction between moderately hydrated polymer molecules and followed heterogenization of the mixture take place under these conditions.

Some additional pecularities of the dependences found may be mentioned. First, as seen, the effect of PVA addition on the viscosity weakens with increasing temperature. It may be connected with the weakening of the influence of each polymer on the hydrophobicity of the other one while heating. Second, despite the fact that on addition of 0.5–4% PVA to a 2% HPMC solution, the viscosity of the system and its heterogenization (see ff.) rises remarkably, the IGT decreases only slightly. So, the IGT of the initial HPMC (Type 1) solution was about 70°C. After addition of the amounts of PVA mentioned, it falls not more than 5–7°C (see data on increasing
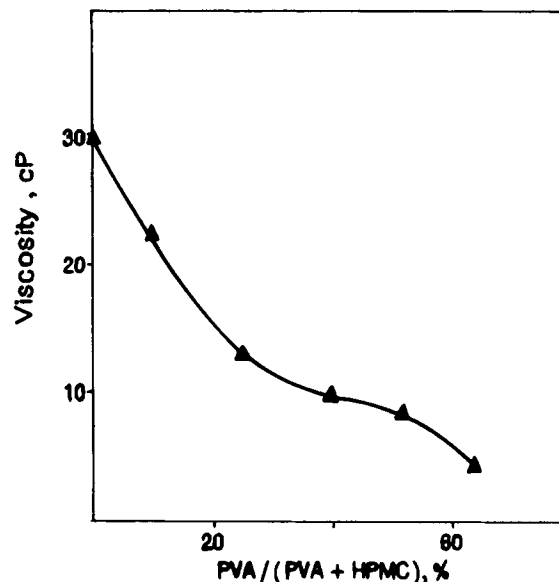
Figure 2   Changes of viscosity for 2% solution of PVA + HPMC (Type 1) as a function of the ratio between them at 55°C. Rate of shear = 32 s^{-1}.

viscosity on heating to 73–65°C in Table III). Besides, the IGT of joint HPMC–PVA solutions considerably exceed the CP of the same ones (less than 30°C). At the same time the IGT and CP of solutions containing only one polymer are very near to each other.[8] The reason for this difference is probably that heterogenization and viscosity increase at low temperatures (less than IGT) are caused primarily by separation of a PVA-rich phase. The main part of HPMC remains unchanged and gels almost independently of the molecular formations present that are responsible for the changes of heterogeneity of the system. It is quite possible that in the processes going on in the system mainly participate in HPMC and PVA molecules having definite structures.

**Table IV   Phase Separation of PVA–HPMC (Type 2) Water Mixtures at 26°C**

| Taken (%)		Found				
		Upper Layer (%)		Lower Layer (%)		Relation Between Upper and Lower Layer
PVA	HPMC	Dry Residue	Vinyl Acetate Units	Dry Residue	Vinyl Acetate Units	
7.75	0.5	4.1	1.3	10.2	4.2	33 : 67
1.9	1.4	2.4	0.4	11.9	4.5	90 : 10
1.1	2.1	2.8	0.25	10.6	4.5	95 : 5

Phase Separation

The heterogenization of PVA–HPMC aqueous solutions was quantitatively characterized by the percent of the "salted-out" lower layer. At constant ratio between both dissolved polymers the lower layer increases with increase of polymers' concentration [Fig. 3(A)]. In these series, the time required for separation into layers increased with increasing concentration (and viscosity) of the system. It is seen from Figure 3(B,C) that low concentrations of HPMC (~ 0.5%) are enough to cause separation of the mixture containing ~ 1% and more PVA into two layers. The amount of salted-out lower layer increases with increase of PVA concentration. At constant concentrations of PVA [Fig. 3(C)] the curve showing the dependence of the heterogenization effect on the amount of added HPMC goes through a maximum, that is, in some conditions the degree of salting-out diminishes with increase of excess of each solute. It can be concluded that the composition of the salted-out products, formed as a result of PVA–HPMC interaction, their hydrophylicity and solubility in water, are determined by the initial ratio of both polymers and their concentrations.

Experiments were undertaken to estimate preliminarily the composition of the salted-out (lower layer) and remaining (upper layer) products. For this purpose, FTIR spectra of HPMC and PVA dissolved in water and also of separate layers of a heterogeneous HPMC–PVA water system were taken (Fig. 4). As seen, spectra of HPMC and PVA dissolved in water differ in the region of C — O stretching and O — H deformation vibrations. HPMC absorbs in the frequency range $1168\text{–}1011$ (1059, 1035) cm^{-1}; PVA, mainly in the range $1315\text{–}1210$ (1277, 1247) cm^{-1} and less in the range $1168\text{–}1011$ cm^{-1}. In the spectra of the separated layers we find peaks related to both polymers. It corroborates the supposition that both phases contain HPMC and PVA.

Data of dry residue and content of PVA vinyl acetate units in both phases are given in Table IV. From this Table one can see that the salted-out products (lower layer) contain 4.2–4.5% of vinyl acetate units. If the composition of the polymers (degrees of substitution and hydrolysis) in both phases were the same, it would mean that the lower layer contains 9.9–10.6% of PVA ($\geq$ 90% of the dry residue). These data are very tentative probably because the fractions of macromolecules of definite molecular weight and composition are salted-out during phase separation. In spite of this, it is clear that in the lower layer PVA dominates.
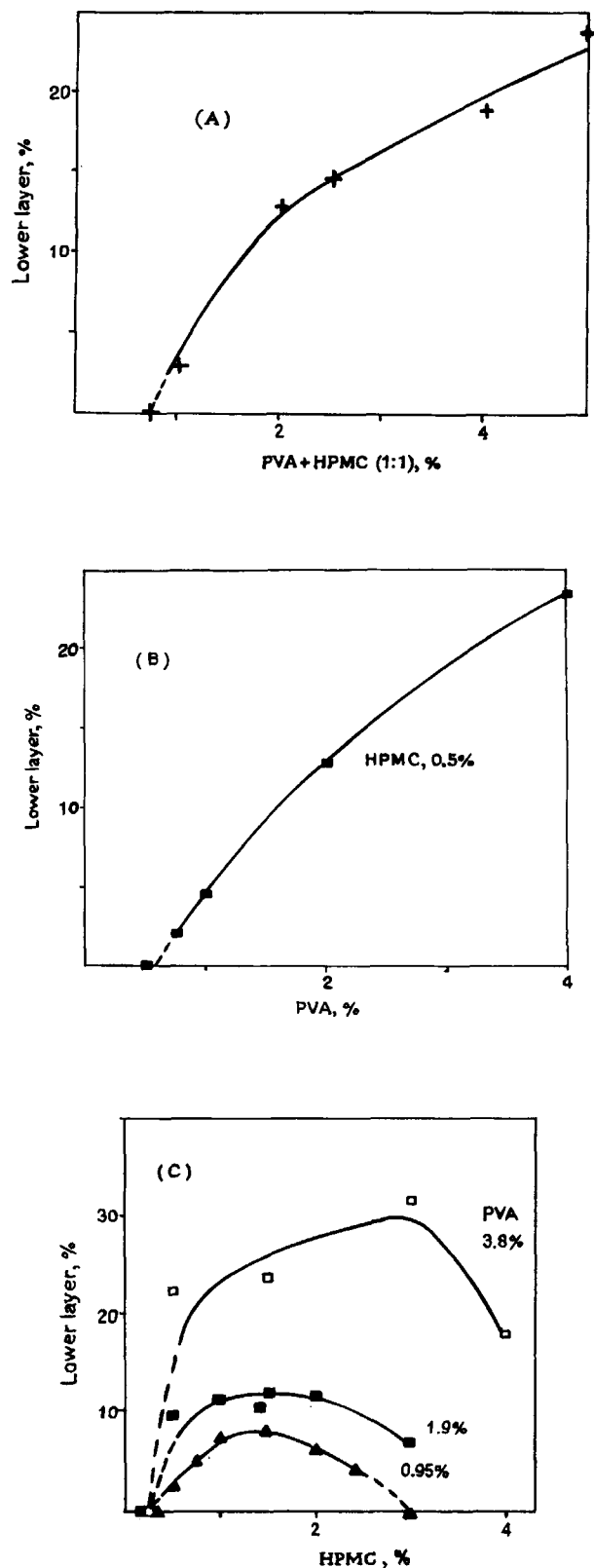
Figure 3   Separation of lower layer from PVA–HPMC (Type 2) water mixtures at 26°C.
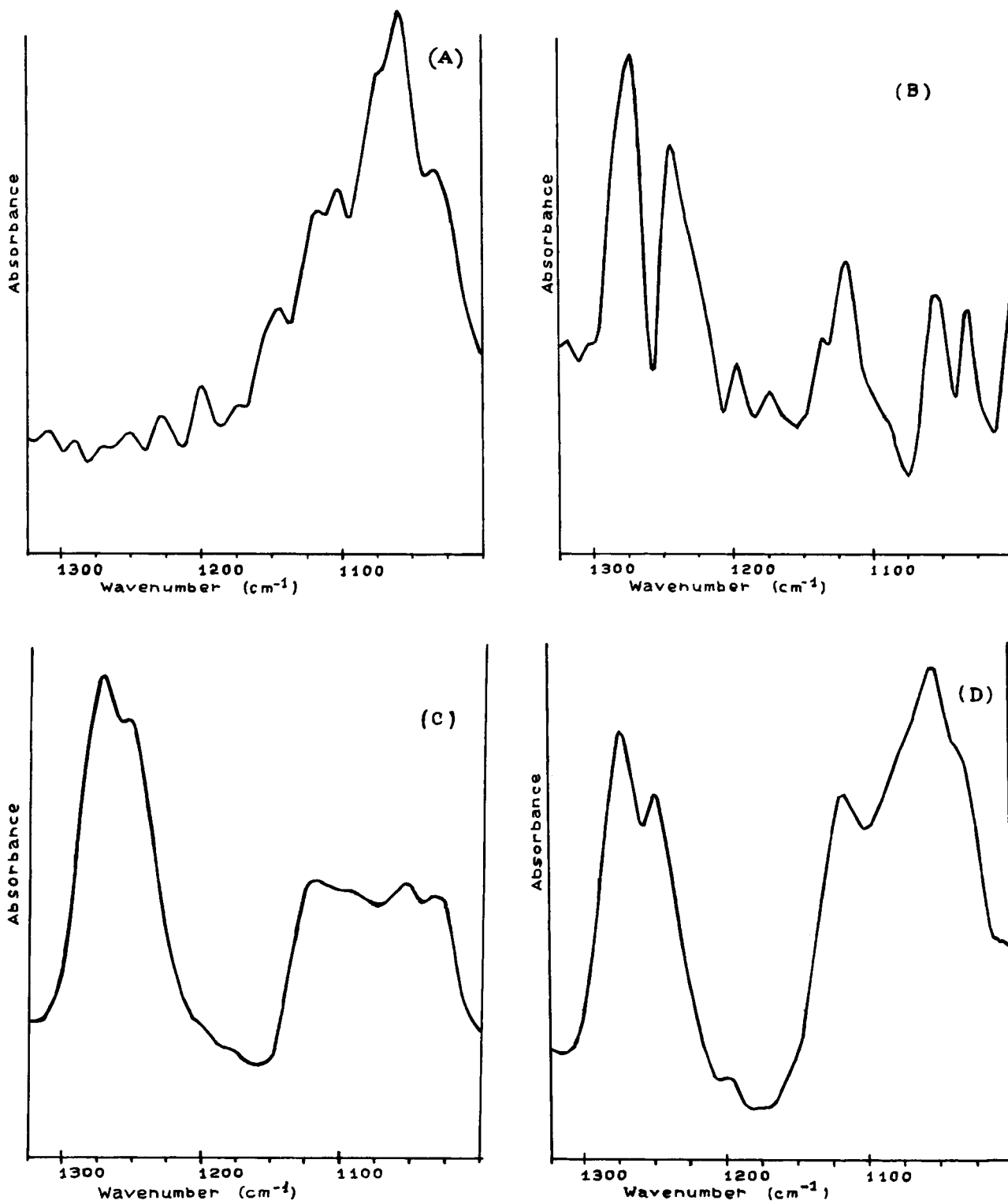
Figure 4 FTIR spectra of HPMC of (A) Type 2, (B) PVA in water solutions, and of solutes in (C) lower and (D) upper layers of heterogeneous HPMC-PVA water mixtures.

Considerations About Vinyl Chloride Polymerization

The data obtained give an insight into the problem of using combined HPMC–PVA dispersants in vinyl chloride polymerization. In the first place, because of different properties of the two polymers, each of them may fulfill definite functions in the polymerization. Using mixtures of dispersants facilitates the systems with desired complexes of properties. In case of the pairs of dispersants studied in this work, HPMC makes it possible to regulate the viscosity of the aqueous solutions and PVA, if necessary, secures their low surface tension. Besides, because of nonadditivity of the properties of HPMC and PVA in aqueous solutions, their common use gives additional possibilities for changing the dispersing power of the aqueous phase during polymerization. The found hydrophobicity increase and more intensive heterogenization when HPMC and PVA are used together may provide stability of the initial dispersion of vinyl chloride in water, and of the suspension formed during polymerization. Undoubtedly, use of HPMC and PVA together helps to make easier regulation of the hydrophylic–hydrophobic balance of the dispersing solution. Because HPMC and PVA, when used together possess reduced hydrophylicity (are less hydrated), it is our opinion that they form more closely packed, more compact, and mechanically stronger protective films and skins around the monomer droplets and polymer particles than each dispersant would separately. This allows the reduction of dispersant amounts used on polymerization, that is, less dispersants are required to achieve given average particle size, particle size distribution, and other properties of polymer particles.

CONCLUSIONS

Interaction of HPMC and PVA dissolved in water leads to viscosity increase and CP decrease of the solutions. On heterogenization of concentrated solutions containing both polymers, lower layers with increased viscosity are formed. They are much more concentrated than the upper layers and are enriched by PVA. It was found that, in spite of CP decrease and separation into immiscible layers of HPMC solutions after addition of PVA, their IGT diminish only insignificantly and are much higher than the corresponding CP. The synergism of viscosity caused by the joint presence of both polymers in aqueous solutions becomes weaker with increase of temperature.

As assumed, the mutual influence of HPMC and PVA molecules in aqueous solutions leads to hydrophobization of the polymers' molecules, that is, to weakening of the solvent–solutes interaction. As a result phase separation intensifies.

Surface tension of dilute HPMC and PVA solutions, in our case, are practically completely determined by the latter polymers' property that is a more active surfactant.

The pecularities caused by the joint presence of HPMC and PVA in the dispersing aqueous solutions may affect the suspension polymerization of vinyl chloride.

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