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ORIGINAL CONTRIBUTION

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The properties of aqueous solutions of some short chain cosurfactants used for radical polymerization of vinyl acetate

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Abstract The refractive index and excess molar volume, of the following short hydrocarbon chain cosurfactants were studied: ethylene glycol, ethylene glycol monomethyl ether, ethanol, *n*-, *i*-propanol, acrylic acid, ethyl monomethylmaleate and acrylamide. The refractive indexes of the aqueous solutions of these compounds vary nonlinearly with composition. The maximum variation of refractive indexes occurs up to a cosurfactant/water molar ratio equal to $\frac{1}{5}$. The fluorescence probe method was successfully used to evidence the structure modifications of the alcohol–water mixtures. The intensity ratio of pyrene fluorescence vibrational bands varies nonlinearly with the composition of the systems; in case of 1-propanol, the sudden decrease of the ratio is similar to that of micellar solutions, so that a critical concentration of association can be determined at a 0.88 water mole fraction. It was shown, in good agreement with data in literature, that the compounds mentioned penetrate into the cluster structure of water and associate. At concentrations higher than critical, restructuring of aqueous solutions continues and structures of bicontinuous or w/o type may arise. The excess volume of the first six compounds is negative owing to the restructuring just mentioned. Vinyl acetate may penetrate in the structures of binary systems to form homogeneous systems. The number of homogeneous systems decreases in the sequence: ethanol, *i*-propanol, acrylic acid, *n*-propanol, the monomethylether of ethyleneglycol, methyl monomaleate. The vinyl acetate over cosurfactant molar ratio of limiting homogeneous systems varies in inverse sequence at the same monomer/water ratio. After radical polymerization of VAc in homogeneous samples transparent systems were obtained only when the polymer was solubilized in cosurfactant water mixtures.

Key words Short chain cosurfactants – refractive index – excess volume – polymerization of vinyl acetate

Introduction

The nanostructure of liquids has been studied in recent papers [1, 2]. The possible existence of a hydrophobic demixtion was evidenced in the case of organic compounds whose chains are too short to form micelles. The hydrophobic effect [3] may also be present in compounds with short hydrocarbonated chains which allows one to obtain short lifetime nanostructures that originate in Brownian motion [1].

These recent results agree very well with earlier data published concerning the aqueous solution of some water-soluble compounds which include short hydrocarbon chains in their structure [4–6]. Thus in aqueous *n*-propanol solutions (*n*PrOH) globular nanostructures were evidenced which possess a 12.4 Å hydrocarbonated zone and 1.8 Å aqueous shell [4]. These structures include 8 moles of *n*PrOH and 40 moles of water (1 mol *n*PrOH/5 mole H_2O). The *i*-propylic (*i*PrOH) and ethylic (EtOH) alcohols exhibit the same association tendency [4].

The study of the dielectric properties of methanol solutions (MeOH), of EtOH and *n*PrOH [5, 6] has indicated that a sudden change occurs at a critical concentration of 1 mol alcohol/5 mol water (the critical fraction of water = 0.83). This sudden change could be assigned to the substitution of a water molecule in its hexagonal clusters by the alcohols in question. At the critical concentration one mole of alcohol replaces a water molecule. These modified clusters still retain the structure of water and may associate [4, 5]. At a concentration higher than critical, the cluster structure of water is destroyed and a "chainlike cluster" structure arises as in case of alcohols. The new structure forms a network by means of hydrogen bonds between chains, the OH groups and water. In fair agreement with Ref. [5] it should be specified that the time scale which affords the discussion on the structures advanced is the picoseconds [1].

The same water destructuring effect is encountered in *i*-propanol (*i*-PrOH), *t*-butanol, ethyleneglycol (EG), acetone and dioxane [6].

Information regarding the structures that may arise at water concentrations lower than critical, could be gained from the study of homogeneous systems that contain methyl methacrylate, acrylic acid (AcrA) and water [7]. Homogeneous systems with o/w, bicontinuous, w/o structures can be obtained by adjusting AcrA/H_2O ratio [7]. This behavior is similar to that of the systems which can micellize [8, 9].

The formation of *i*PrOH, hexane, water microemulsions without surfactant is possible because of the association of alcohol which thus creates predominantly hydrocarbonate and aqueous zones [10–14].

The water-soluble alcohols (1–4 carbon atoms) may act as cosurfactants efficient in obtaining microemulsions in presence of surfactants [15–18]. Therefore, the compounds studied are hereafter referred to as "short chain cosurfactants" (SCC).

The interfacial properties of SCC aqueous solutions [19–21] exhibit a sudden change over the range of water critical concentration just because of their nanostructuring.

This contribution deals with the properties of aqueous solutions of some alcohol-type SCCs; measurements of refractive index, fluorescence and excess molar volume were carried out. Because the authors are interested in the polymerization of some vinyl monomers in SCC aqueous solutions [22–24], several polymerizable SCCs are also studied: acrylic acid, ethyl monomaleate (MEMEt), and acrylamide (AA). The polymerization of vinyl acetate (VAc) in these SCC/H_2O systems was also studied.

Experimental

Materials

Ethanol, *i*-propanol, ethyleneglycol, acrylic acid, vinyl acetate commercial products were purified by rectifying. Monomethyl ethyleneglycol ether (EGMME), Merck product, was utilized without further purification. Acrylamide was purified by recrystallization. Ethyl monomaleate resulted from the reaction of an equimolar mixture of maleic anhydride and ethanol dried on molecular seives. The reaction was conducted three hours at 60 °C. The conversion determined by titration was 98.5%. The structure was verified by NMR. Pyrene (Aldrich Chem. Co.) was recrystallized twice from ethanol. The pyrene concentration in water, alcohol and their mixtures was less than 10^{-6} M.

Methods

The refractive index was measured at 25 °C by means of an Abbe refractometer. The molar volume of mixtures (V_m) was calculated by means of the average molecular weight over density ratio, at 20 °C [25, 26]:

$$V_m = (M_1 x_1 + M_2 x_2)/\rho ,$$

where M_1, M_2 stand for the molecular weights of single components, ρ for the density of mixtures and x_1, x_2 for the molar fractions of components 1 and 2.

The molar excess volumes (ΔV_E) of mixtures are:

$$\Delta V_E = V_m - V_1 x_1 - V_2 x_2 ,$$

where V_1 and V_2 are the molar volumes of the components.

The ternary diagrams were obtained as in previous contributions [24, 27].

Five VAc/SCC (o) mixtures were prepared: 9/1; 7/3; 5/5; 3/7; 1/9 weight. Nine systems of weight ratios 1/9–9/1 with water (w) were prepared from each mixture. After stirring and 24 h equilibration at 20 °C the 45 systems were visually analyzed. The number of homogeneous samples obtained is mentioned in Fig. 6.

The fluorescence probe method is based on the variation of fluorescence probe properties as function of the nature of its microenvironment. Thus, the ratio of the intensities of first and third pyrene vibrational bands in the fluorescence spectrum of the monomer depends on the nature of the solvent; there is an obvious correlation between the value of the ratio and the polarity of the solvent [28, 29]. This feature is employed in the case of micellar solutions to determine the critical micellar concentration (CMC) [30]. At concentrations lower than CMC pyrene lies in water and I_1/I_3 ratio is 1.79 (the value differs depending on the characteristics of the equipment employed, the resolution, slit, increment and spectrum correction). After micellization pyrene is solubilized in the hydrophobic core of the micelle and the ratio decreases markedly, which indicates the transfer of pyrene from a more polar to a less polar environment. The steady-state fluorescence sectra were recorded on a Shimadzu RF-5001 PC spectrofluorophotometer. The spectra were corrected and the slits narrow (0.1 mm, at emission monochromator); $\lambda_{ex} = 330$ mm. The measurements were carried out at 25 °C.

Results and discussion

Short chain surfactant–water mixtures

The study of vinyl acetate microemulsions containing EtOH, *n*PrOH, H_2O, surfactant has shown that the refractive indexes of the homogeneous mixtures depend nonlinearly on the ratio of organic to aqueous phases [24, 31]. This behavior was encountered in SCC/H_2O mixtures rather than in VAc/SCC ones, which suggested one to assign it to water destructuring [5, 6] followed by nanostructuring of SCC/H_2O systems [4].

The dependence of refractive indexes of SCC/H_2O mixture on the mole fraction of the organic compound (f_1) is shown in Fig. 1; note that all compounds studied exhibit a nonlinear dependence on the composition of mixtures. In SCC/H_2O systems with water molar fraction lower than 0.83 the hydrocarbon domains are present. Owing to the existence of these domains of higher refractive index, the modifications of the refractive index of the mixture are not significantly affected by dilution with water. At a water molar fraction higher than 0.83 the hydrocarbon domains are destroyed and the value of the refractive indexes drop to the value of water index. In the VAc/SCC systems a linear modification of the refractive index of f_1 occurs owing to the absence of the hydrophobic demixtion. The pronounced change at critical mole fraction ($f_1 = 0.17$) was also evidenced by other methods [4–6]. The existence of this nonlinear change allows one to conclude that a nanostructuring occurs in all systems studied [1, 2, 4].

The nonlinear variation of the I_1/I_3 ratio of pyrene fluorescence with composition has also suggested the nanostructuring of SCC/H_2O system. Figure 2 shows the fluorescence spectrum of pyrene in 70% H_2O–30% *n*-propanol solution (molar fraction of water 0.88); one can note five bands of pyrene fluorescence vibrational structure. Figure 3 shows the dependence of I_1/I_3 ratio on mole fraction of organic compound, f_1 in case of water–*n*-propanol, water–ethanol and water–methanol mixtures. In case of water–*n*-propanol solutions, the decline of the ratio occurs suddenly, a behavior which is very similar to that of micellizable surfactants. One can even determine by analogy a critical concentration of association of about 0.12, a value in good agreement with that resulted from light scattering [4]. The shape of the curves is similar to that

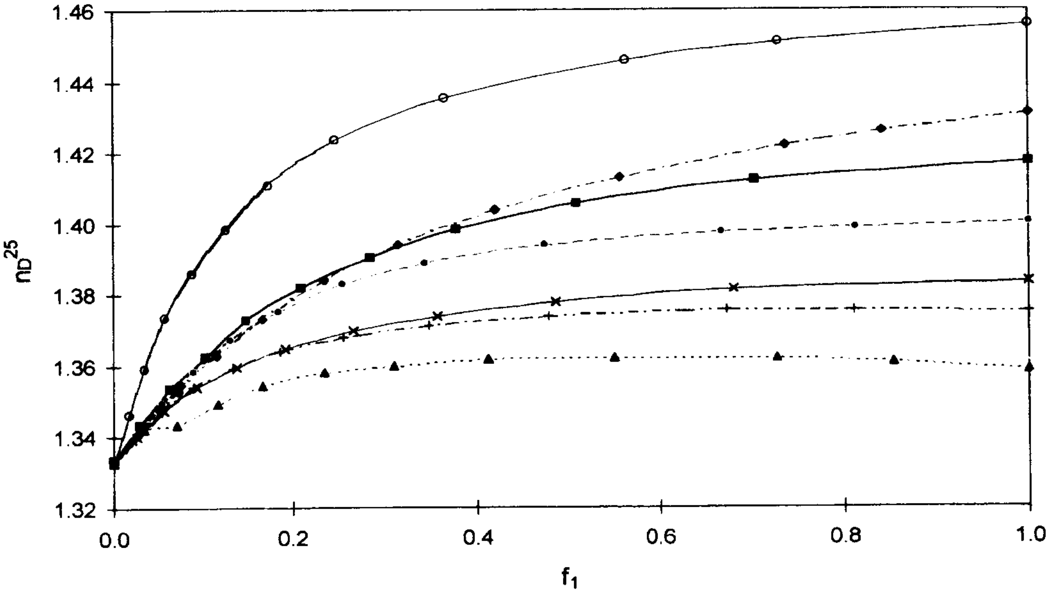


Fig. 1 Modification of refractive indexes in SCC/H_2O system (f_1 = mole fraction of SCC) at 25 °C (—■— AcrA, —▲— EtOH, —●— EGMME, —▼— MEMEt, —◆— EG, —+— *i*-PrOH, —×— *n*-PrOH)

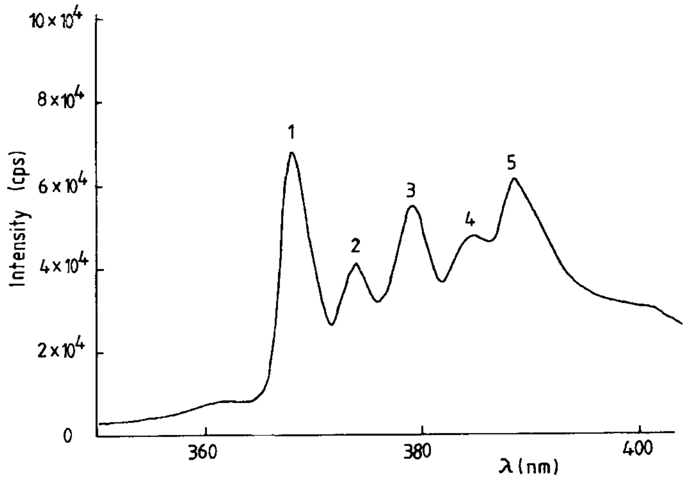


Fig. 2 The fluorescence spectrum of pyrene monomer in 30% 1-propanol and 70% water

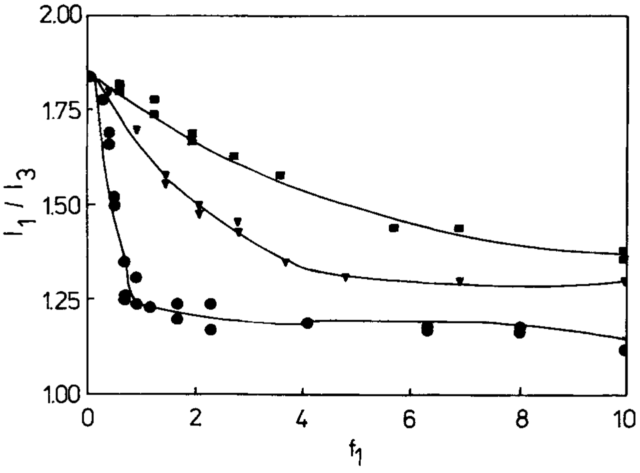


Fig. 3 The I_1/I_3 ratio of the intensities of pyrene fluorescence vibrational bands versus molar fraction, f_1

resulted from light scattering. In methanol the decrease of I_1/I_3 ratio is slower (perhaps the probe is too large for those small associates); it is linear up to a molar fraction of 0.50, then its value remains constant. In ethylic alcohol the behavior of pyrene is intermediary; it is also possible to estimate a critical concentration at about 0.40 mol fraction. Our results also confirm the conclusions drawn in Ref. [5], which deals with a study carried out by microwave dielectric method; this method evidenced a structure change at $f_w = 0.83$, for n-propanol.

These results are very important for scientist involved in polymer science because they proved that AcrA or MEMEt-type polar monomers may initially generate nanostructured systems. Bicontinuous or w/o [7] structures may appear at concentrations higher than critical.

The most important monomer of this kind is acrylamide. It was extensively studied in inverse microemulsions [32]. Most systems that form inverse microemulsions exhibit a AA/H_2O ratio higher than the critical concentration. It turns out that the systems in question contain destructured water. Destructuring of water was demonstrated by NMR studies [33]. The progressive association of AA molecule as its water concentration increases [34] proves that it behave similarly with other SCC [4–6]. An additional proof for the association capacity of AA in water is represented by the nonlinear dependence of refractive indexes of its aqueous solutions on mole fraction (Fig. 4). Because AA is solid above a certain concentration the investigation could not be extended.

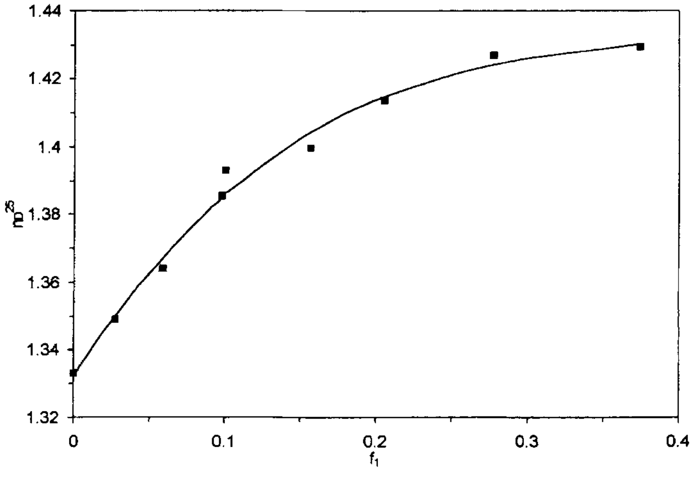
The variation of the molar excess volume of SCC aqueous solutions studied is shown in Fig. 5.

The ΔV_E values of all water solutions of the compounds studied were negative which suggests that they undergo contraction on mixing (Fig. 5). The difference between ΔV_E values changes after the critical concentration ($f_1 = 0.17$) was reached. The volume contraction continues at concentrations higher than critical, allowing the SCC molecules to organize in a way other than globular (4), like the surfactants [8, 9]. The possible formation of a bicontinuous structure was evidenced in case of AcrA [7]. It is supported by the existence of a maximum of viscosity over the concentration range within which a minimum of ΔV_E or bicontinuous structures are present [25, 35].

In compounds with CHOH common group the sequence of excess molar volume of various substitutents is

$$\genfrac{}{}{0pt}{}{-\mathrm{H}}{-\mathrm{CH_3}} > \genfrac{}{}{0pt}{}{-\mathrm{H}}{-\mathrm{CH_2OCH_3}} > \genfrac{}{}{0pt}{}{-\mathrm{CH_3}}{-\mathrm{CH_3}} > \genfrac{}{}{0pt}{}{-\mathrm{H}}{-\mathrm{CH_2CH_3}} > \genfrac{}{}{0pt}{}{-\mathrm{H}}{-\mathrm{CH_2OH}}\,.$$

Fig. 4 The variation of refractive index in acrylamide–water system versus molar fraction, f_1



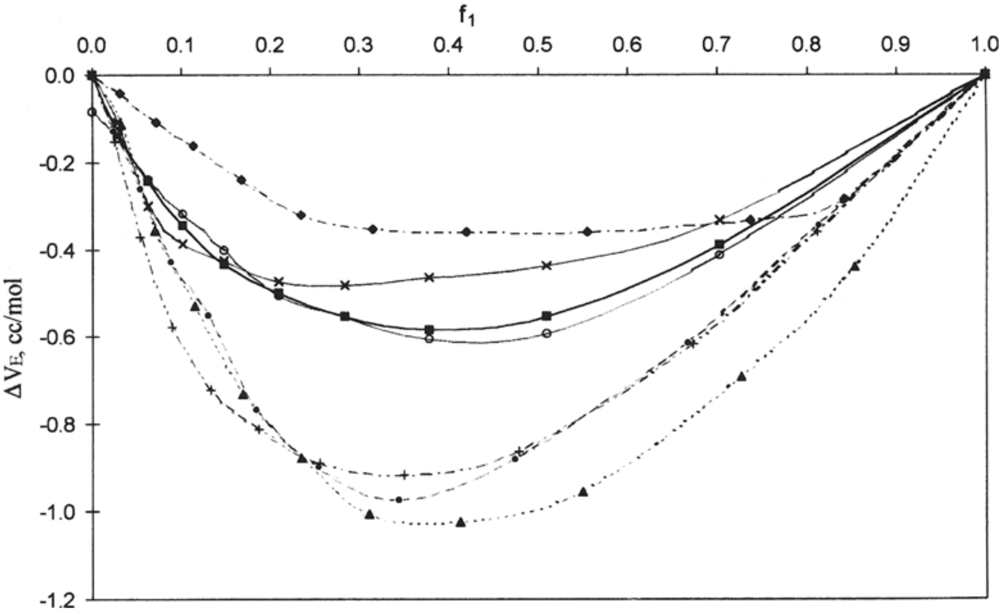


Fig. 5 The molar excess volume versus the molar fraction of the organic compound, f_1, for aqueous solutions, at 25 °C. The symbols are the same as in Fig. 1

It is surprising to note that the minimum ΔV_E value is encountered in the most hydrophilic and hydrophobic substituents. The ΔV_E value results from the following cumulated effects [25]: the breaking up of hydrogen bonds in the initial compounds, the formation of new hydrogen bonds between the molecules of the two compounds in solutions and their interstitial ordering. In case of ethyleneglycol, the initial intermolecular bonds of the compound are very strong owing to the OH groups. The mixtures with water cannot ensure an important strengthening of these bonds and, consequently, results in an increased contraction. In case of *n*PrOH, the *n*-propyl group is too long to afford an enhanced interpenetration of the two types of molecule and an increase of intermolecular hydrogen bonds in aqueous solutions. According to the nanostructure model advanced by Grossman [4], the *i*-propyl group may reach an increased interstitial ordering [25]. These results are in good agreement with those recently published [36].

The two polymerizable SCC, AcrA and MEMEt, possess very strong intermolecular hydrogen bonds. Like in the case of EG, because of these strong hydrogen bonds, the density of these low ΔV_E compounds is high.

Ternary phase diagrams (VAc/SCC/H_2O)

In case of polymerization processes it is important to know how the solutions of the compounds studied may produce homogeneous systems in presence of the usual monomers. In this contribution vinyl acetate was used as monomer. The number of homogeneous samples is presented in Fig. 6. Of the 45 systems studied the largest number of homogeneous phases was obtained in EtOH (18) and the lowest in MEMEt (13). The homogeneous system forming capacity depends on the possibility that VAc penetrates into the nanostructured systems of SCC. EG could not have been studied because it is not compatible with VAc in any proportion.

The line that links VAc corner with SCC/H_2O = 1/5 mol/mol critical concentration divides the triangle in question into two zones. The zone opposite to the H_2O corner corresponds to the composition of lower than critical SCC concentration. The higher zone, next to towards SCC corner corresponds to some concentrations higher than critical. In this zone bicontinuous and w/o structure show up. Barden et al. [14] referred to these system as "detergentless water/oil microemulsions". These microemulsions originate in the cosurfactant association rather than surfactant association. Examination of VAc/SCC/H_2O molar ratios in the compositions of homogeneous samples presented in Fig. 6 shows that, at the same VAc/H_2O ratio, the efficiency is inversely proportional to the number of homogeneous phases.

For o/w = 5/5 the homogeneous samples correspond to a VAc/SCC/H_2O molar ratio equal to 1/4.35/15.9 (EtOH); 1/3.32/15.9(*i*-PrOH). In case of EtOH a VAc/SCC molar ratio higher than *i*PrOH is required. These results are in good agreement with those shown in Fig. 3. In order to include hydrophobic molecules in the SCC/H_2O system a hydrophobic microenvironment has to be ensured. Cosurfactants with shorter hydrocarbon chain require a

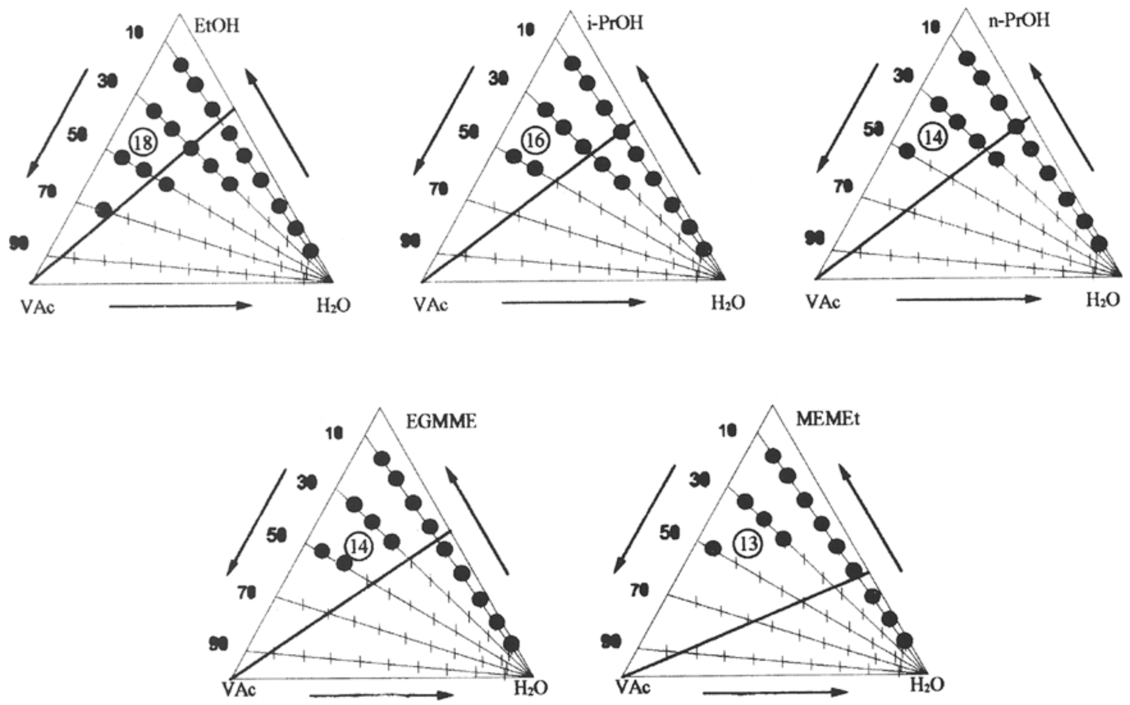


Fig. 6 Ternary phase diagrams $VAc/SCC/H_2O$ (o-homogeneous samples; x-separate phases)

Table 1 Influence of the initial composition and of SCC on the final solid contents (%) and on the number of final homogeneous samples ( ); 24 h, 65 °C

o_0 VAc/SCC	o_0/w_0	$VAc/SCC/H_2O$ (% w)	% Solid content of final homogeneous samples				
			EtOH (15)*⁾	*i*-PrOH (15)	*n*-PrOH (12)	EGMME (4)	MEMEt (10)
30/70	90/10	27/63/10	21.4	17.15	22.7	25	65.7
	80/20	24/56/20	21.0	15.15	18.9		34.0
	70/30	21/49/30	18.4	14.40	14.8		25.0
	60/40	18/42/40	16.0	13.00	14.4		
50/50	90/10	45/45/10	41.4	37.00	43.4	45	82.0
	80/20	40/40/20	38.0	35.00			
	70/30	35/35/30	33.4				

*⁾ Number of final homogeneous samples.

larger number of shorter methanol (Fig. 3) or ethanol (Fig. 6) molecules than in the case of propanol.

Polymerization of vinyl acetate in homogeneous samples

After polymerization not all initially homogeneous systems retain this feature. The number of homogeneous samples after polymerization is mentioned for each SCC ( ) in Table 1. The initial compositions which ensured the homogeneity and the final polymer content are also mentioned in the Table 1.

Analysis of the polymer content in the systems mentioned reveals that the *i*-PrOH yields the minimal conversion of VAc. This phenomenon can be accounted for by the degradative chain transfer undergone by the growing macroradical or the radical resulted from the initiator decomposition. In the case of *i*-PrOH this transfer [23] results in a less active tertiary radical which fact is also demonstrated by the molecular weights of the polymer obtained. For a system with VAc/SCC = 30/70 and $o_0/w_0 = 60/40$ the molecular weights decrease as such

i-PrOH (4000) < EtOH (11 100) < *n*-PrOH (15 700) .

The polymer-cosurfactant compatibility [37] plays an important part in the stability of the system obtained after polymerization in microemulsion. Poly(vinyl acetate) is soluble in alcohol–water mixtures [38]; this is the case of EtOH, PrOH. In case of EGMME, the compatibility is probably much lower and therefore the number of homogeneous final samples is lowest, although the monomer conversion is maximum.

The reactivity of MEMEt brings about the increase of polymer content compared to the other cosurfactants. As a result of the low reactivity of maleic group its conversion is not complete.

The systems which are initially homogeneous at any water content and those whose VAc/SCC = 10/90 retain their homogeneity after polymerization in case of EtOH and *i*-PrOH. The conversion does not exceed 10%. In the case of EGMME higher conversion brings about phase separation and the systems whose initial composition was $o_0/w_0 = 90/10$; 80/20 remain homogeneous. MEMEt stable systems are obtained for $o_0/w_0 = 90/10 \div 40/60$. In this case the conversions reach maximum 30%.

In conclusion, one can affirm that the system of cosurfactants with short chain studied form homogeneous systems with water; their refractive indexes and excess volume as well as fluorescence properties of the probe (pyrene) do not depend linearly on composition. This behavior supports the nanostructuring of these systems. Even the hydrocarbonate short chains can yield a hydrophobic-type association Vinyl acetate can form homogeneous VAc/SCC/H_2O systems. The sequence of their decreasing number is as follows: EtOH > *i*-PrOH > AcrA > *n*-PrOH > EGMME > MEMEt.

After radical polymerization of vinyl acetate in the homogeneous samples this property is retained only when the polymer is solubilized in cosurfactant–water mixture. The cosurfactant acts as chain-transfer agent.

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