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ORIGINAL CONTRIBUTION

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Polymerization of vinyl acetate in homogeneous systems obtained in presence of acrylic acid

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Abstract The composition ranges over which microemulsions are formed in systems containing vinyl acetate, acrylic acid, water with nonylphenol ethoxylated with 25 mol ethylene oxide monomaleate as surfactant were studied. Conductometric and refractometric investigations have shown the existence of some aqueous/organic, bicontinuous and organic/aqueous microemulsions. The types of precursor microemulsions influence the conversion of monomers. In the presence of a crosslinking agent, diethylene glycol bis maleate, hydrogels are formed whose water absorption depends on the composition of the initial microemulsions. The kinetics of water absorption suggests the modification of polymer network structures as a function of the crosslinked monomer content and the ratio of organic to aqueous phases.

Key words Microemulsions – Vinylacetate – Acrylic acid structure – Polymerization

Introduction

Acrylic acid (AcrA) is an efficient cosurfactant suitable for obtaining microemulsions of polar monomers [1–4]. Methacrylic acid is less efficient than AcrA [4]. Microemulsions can be prepared in the presence as well as in the absence of surfactants [1, 2, 4]. Microemulsions may be obtained in the absence of surfactants making use of other short-chain cosurfactants (SCC), for example isopropanol [5–9]. Formation of this type of microemulsion should be assigned to the nanostructuring capacity [10, 11] of SCC in aqueous solutions [12–14]. The SCC hydrocarbon chains can be associated with the production of preponderantly hydrocarbon and aqueous [12–15] zones in the homogeneous systems formed in a way similar to the surfactants [16, 17].

In a previous study it was shown that some physicochemical properties of SCC-water systems depend nonlinearly on the ratio of the two components, a behavior which is assigned to nanostructuring [18]. Starting from these results, this contribution focuses on the homogeneity domains obtained for vinyl acetate (VAc)-AcrA-H_2O or VAc-AcrA-H_2O-surfactant systems. The modification of VAc and AcrA monomer conversions in radical polymerization and the possibility to obtain gels by introducing a crosslinked monomer were studied in the homogeneous systems obtained.

Experimental

VAc and AcrA commercial products were purified by rectification. Benzoyl peroxide "Chimopar" was utilized without purification. The surfactant, nonylphenol monomaleate ethoxylated with 25 mol ethylene oxide ($MEMNPEO_{25}$) and the crosslinking agent, bis maleate diethylene glycol (MDEGM) were prepared in the laboratory. $MEMNPEO_{25}$ was prepared from maleic anhydride and nonylphenol ethoxylated with 25 mol ethylene oxide ($NPEO_{25}$), molar ratio 1/1; MDEGM was prepared from maleic anhydride and diethylene glycol, molar ratio 2/1. The reaction took place at 60 °C and lasted 3 h. The conversion exceeded 98%. Testing of esterification was carried out by titration of final COOH groups. The structure was verified by ^{1}H NMR.

The homogeneity ranges were selected from 45 systems of various compositions [18–20]. The initial systems were obtained by mixing some organic (o) and aqueous (w) phases in nine gravimetric ratios 1/9–9/1.

The aqueous phases were distilled water or aqueous solutions of surfactant (33% $MEMNPEO_{25}$). The organic phases consisted of five VAc/AcrA solutions of gravimetric ratios ranging within 10/90–90/10. In reticulated systems MDEGM was introduced in a gravimetric ratio of 5% or 10%. After mixing organic and aqueous phases, the homogeneous systems were selected visually.

The refractive indexes (n_D^{25}) and conductivities (χ) of the homogeneous systems were measured at 25 °C by means of an Abbé refractometer and a Radelkis conductometer, respectively.

The molar excess volume (ΔV_E) was calculated by the equations

$$V_E = V_m - V_1 x_1 - V_2 x_2 \qquad (1)$$

$$V_m = (M_1 x_1 + M_2 x_2)/\rho \ , \qquad (2)$$

where V_m stands for the molar volume of the mixture, ρ for the density of the mixture, x_1, x_2 and M_1, M_2 for the mole fraction and molar masses, respectively, of the components, and V_1 and V_2 are the molar volumes of the components at 25 °C.

The swelling of the polymers was determined by immersing dry polymer cylinders of about 0.5 g in water at room temperature. The degree of polymer swelling (S) was established by weighing the initial amounts of polymer (m_0) and of polymer with water absorbed (m_t) at various time intervals, t.

The equilibrium value for the degree of polymer swelling was determined after 96 h.

$$S = (m_t - m_0)/m_0 \qquad (3)$$

Polymerization of homogeneous systems was effected at 65 °C over 24 h in flame-sealed glass phials. The systems contained 0.2% initiator with respect to (VAc + AcrA). The final conversion of the two monomers was determined by gravimetry.

Results and discussion

The possibility to form microemulsions with SCC for acrylic [1–4] and vinylic [18–20] monomers by means of ternary diagrams was studied in previous works. AcrA and metacrylic acid [1–4] as well as alcohols [18–20] were utilized as SCC.

This paper reports the first system containing VAc as a monomer and AcrA as a SCC. An attempt was made to fit the results of other authors [1–4] with ours accounting for the causes which produce solubilization of the polar monomers in SCC-containing microemulsions.

In a mixture with water AcrA behaves similarly to a SCC-type alcohol [18]. In the case of alcohols it is definitively proven that at a critical concentration corresponding to a ratio of 1 mol SCC/5 mol H_2O the properties of mixtures change suddenly [13, 14]. In the case of propanol at the same concentration globular formations which contain 8 mol alcohol and 40 mol water were found [12].

The composition ranges of homogeneous systems are shown in Fig. 1. The VAc-AcrA-H_2O system (Fig. 1a) exhibits homogeneity ranges at concentrations close to those which contain propanol instead of AcrA [18]. The critical concentration, 1 mol AcrA/5 mol H_2O, corresponds to 56% weight of H_2O in the AcrA/H_2O mixture [13]. The concentrations of water in most of the homogeneous systems, except 10/90 VAc/AcrA mixtures, are lower than the critical concentration. At this critical concentration a SCC molecule replaces a water molecule in the hexagonal clusters of water [13, 14] and may associate as globular nanostructured systems [12]. Thus the possibility is created that hydrophobic zones are formed within which a third component, whose solubility in water is limited, may solubilize [18]. Comparison with the study regarding methyl methacrylate [1–4] suggests that most homogeneous systems in Fig. 1a possess a bicontinuous or w/o-type structure, owing to the low concentration of water.

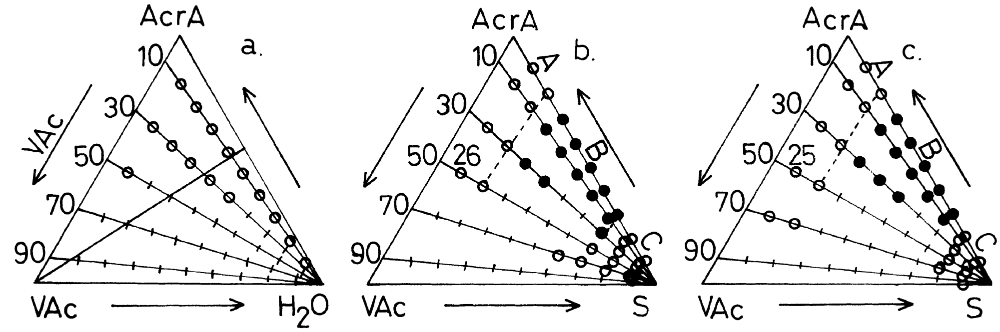

Fig. 1 Ternary diagrams for the vinyl acetate (VAc)/acrylic acid (AcrA) systems. **a** VAc/AcrA/H_2O, **b** VAc/AcrA/S and **c** VAc/AcrA/S (5%MDEGM) (S = 33% nonylphenol monomaleate ethoxylated with 25 mol ethylene oxide, ● represents a bicontinuous structure)

The presence of surfactant (Fig. 1b) modifies the concentration ranges of homogeneous systems. The possibility arises that some o/w systems show up in an aqueous phase-rich range. Therefore the number of homogeneous phases shown in the diagram is much higher than in the absence of $MEMNPEO_{25}$ (Fig. 1a). The presence of MDEGM (Fig. 1c) does not significantly alter the concentration range and the number of homogeneous phases. The ternary diagram of the 10% MDEGM system was not plotted.

The structure modifications of the homogeneous systems initially obtained were determined by physico-chemical analyses which have proved their efficiency in other systems [1–4, 18, 19]. These properties were determined as functions of the weight fraction of the aqueous phase [$x = w/(w + o)$]. The results obtained in the AcrA-H_2O system are shown in Fig. 2.

As in case of other SCC [18], their presence in water exhibits a negative variation with a minimum for ΔV_E and a nonlinear modification of n_D^{25} with x. These changes are assigned to "hydrophobic demixtion" [10–12, 15] induced by the hydrocarbon chain of the SCC. Over the $x = 1$–0.56 range, AcrA associates through its hydrocarbon chain and produces the most dramatic alteration of ΔV_E and n_D^{25} as its concentration increases. The derivatives of the curves representing this variation are constant and take extreme values ($d\Delta V_E/dx$; dn_D^{25}/dx).

At $x = 0.56$ a molar ratio of 1 mol AcrA/5 mol H_2O is reached at which associated systems are formed [12–14] as in the case of surfactants [16, 17]. Above this concentration, association of SCC with water continues; yet the effect of this process is not that efficient in modifying the physico-chemical properties. The $d\Delta V_E/dx$ and dn_D^{25}/dx values exceed the extreme value.

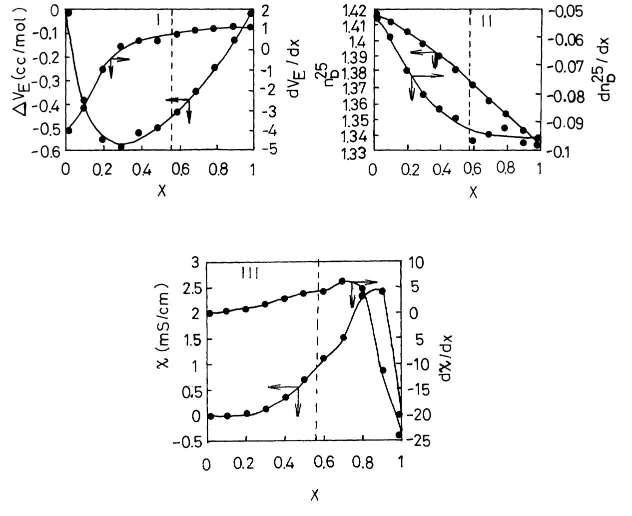

Fig. 2 Modification of **I** excess molar volume, **II** refractive indexes and **III** conductivity in ArcA/H_2O mixtures

The modification of the conductivity in the AcrA/H_2O mixture supports the statements mentioned above (Fig. 2III). At low AcrA concentrations ($x = 1$–0.9) the conductivity increases with increasing SCC concentration because the number of dissociated ions increases. Further increase of AcrA concentration lowers the conductivity because the ionic attractions are stronger and, although the overall number of ions increases, the number of active ions decreases. Additional information may be obtained by tracing the differential curve ($d\chi/dx$) (Fig. 2III). The significant modification of this curve occurs before the critical concentration is reached ($x = 0.56$). As soon as this modification is reached, the decrease (increase of AcrA concentration) is minimum and tends to zero. It turns out that further increase over the AcrA critical concentration does not significantly modify the conductivity; this could be explained by the formation of bicontinuous- or w/o-type structures [1–4, 16, 17].

In the VAc-AcrA-H_2O ternary diagrams (Fig. 1a) solubilization of large amounts of VAc occurs at AcrA concentrations that exceed the critical concentration. Physico-chemical modifications (Fig. 2) and the solubilization domains of VAc support the previous assumption that under the conditions shown in Fig. 1a the microemulsions formed adopt a bicontinuous-type structure and w/o. Thus it is explained for the first time why AcrA can form a "detergentless microemulsion" [1–4] similar to other SCC [5–9].

The presence of a nonionic surfactant in the aqueous phase ($NPEO_{25}$) alters the SCC association in water (Fig. 3). The refractive indexes also depend nonlinearly on composition, while the conductivity at first increases with increasing AcrA concentration and then decreases. The distinction is evidenced by the dn_D^{25}/dx curve: no constant maximum value is obtained between $x = 1 - x_{critical}$ (Fig. 3I). In the case of AcrA, the critical concentration corresponds to $x = 0.47$. The presence of a hydrophobic zone in the surfactant solution allows AcrA to be enclosed in the structures existing in the aqueous phase; therefore the increase in refractive index with increasing SCC concentration is no longer constant up to the critical concentration.

The modification of the conductivity with x in the presence of $NPEO_{25}$ (Fig. 3II) is similar to that of the system without surfactant (Fig. 2III); however, after exceeding x_{cr} the differential curve records a more pronounced change when x decreases.

The systems which are interesting for polymerization are those shown in Fig. 4. The refractive indexes decrease nonlinearly with increasing x when the organic phase is AcrA or AcrA/VAc = 90/10, 70/30 solutions (Fig. 4I). In aqueous media SCC autoassociates and owing to "hydrophobic demixtion" [10, 11] zones with strongly hydrocarbon character are formed. Therefore the refractive indexes increase more than in ideal

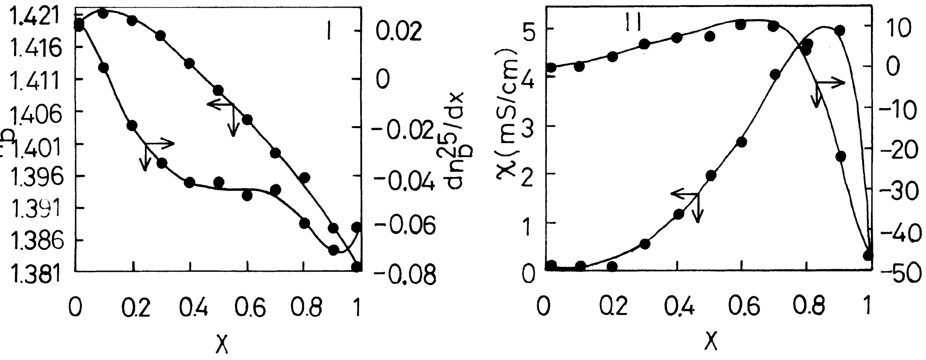

Fig. 3 Modification of **I** conductivity and **II** refractive indexes in AcrA + nonylphenol ethoxylated with 25 mol ethylene oxide (33%) systems

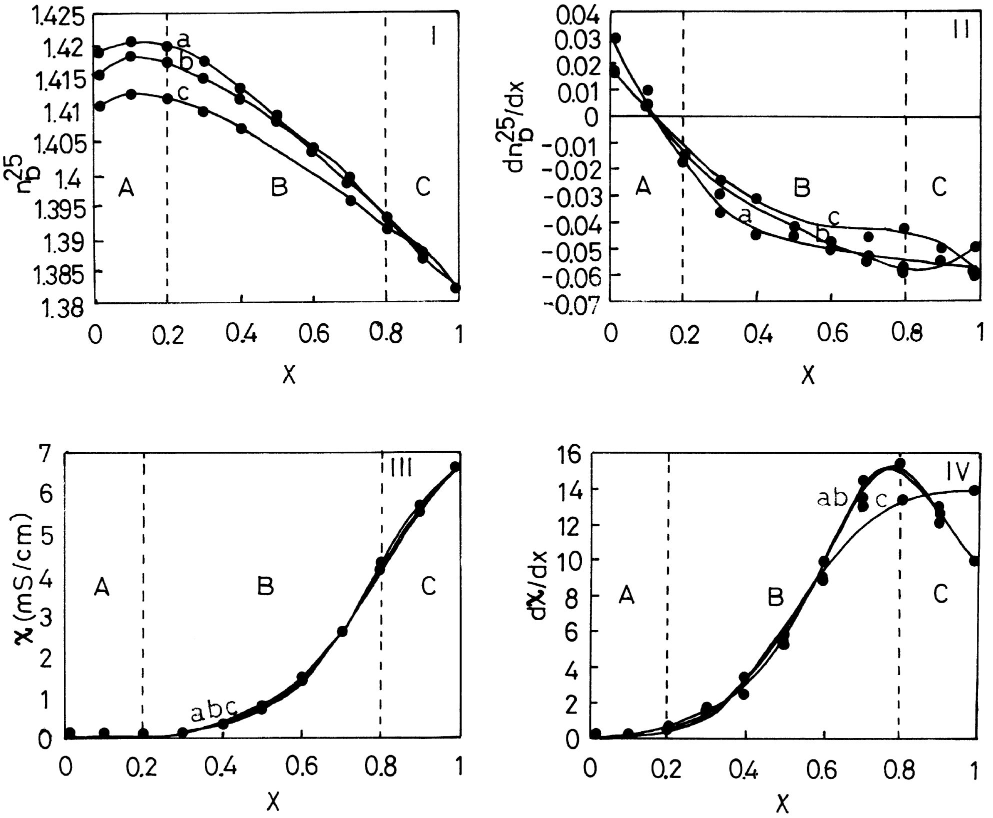

Fig. 4 Modification of **I, II** refractive indexes and **III, IV** conductivity with mole fraction x in the systems shown in Fig. 1b [x = w/(w + o)]; VAc/AcrA = 0/100 (*a*), 10/90 (*b*), 30/70 (*c*)

solutions [18–20]. The nonlinearity of the refractive index modification with the decrease of aqueous phase concentration points to nanostructuring [18], a phenomenon which is preserved in the presence of the surfactant [20]. The variation of $\mathrm{d}n_{\mathrm{D}}^{25}/\mathrm{d}x$ versus x (Fig. 4II) occurs as in the case of nonionic surfactant (Fig. 3I). Three distinct zones can be noted.

The reactive surfactant, MEMNPEO$_{25}$, possesses an ionizable COOH group which confers a high conductivity on the aqueous phase (Fig. 4III). The presence of AcrA does not result in an increase in conductivity, not even at low concentrations. The existence of some groups dissociated from the beginning and originating in the surfactant no longer favors dissociation of SCC molecules. AcrA is included in the initially structured system of the MEMNPEO$_{25}$ solution. The presence of VAc does not modify the conductivity (Fig. 4III).

The modification of the conductivity evidences the existence of three distinct zones, as in the case of MMA-containing [1, 2, 4] systems. A clearer definition of the three zones may be achieved by means of $\mathrm{d}\chi/\mathrm{d}x = f(x)$ (Fig. 4IV). These three distinct zones prove the existence of structural changes in the apparently homogeneous systems obtained. They are in fact microemulsions of w/o-(A), bicontinuous-(B), and o/w-(C) [1, 2, 4] type. The three distinct zones are shown in Fig. 4 and in the ternary diagrams (Fig. 1b, c). The microemulsions obtained with MEMNPEO$_{25}$ (33%), which contain o/w = 9/1, 8/2 possess water-in-oil structure, while those with o/w = 2/8, 1/9 have oil-in-water structure. The intermediate compositions possess a bicontinuous structure.

After polymerization, the initially homogeneous systems obtained without surfactant retain this property. All systems, except those with VAc/AcrA = 10/90, retain their initial homogeneity only over the low concentration of the aqueous phase. These systems correspond to bicontinuous or w/o initial structure. This is a first distinction from the systems obtained in the presence of alcohols and MEMNPEO$_{25}$ [20]. A second distinction from SCC nonreactive systems is the modification of the conversion as a function of initial composition (Fig. 5).

In all cases studied the final conversion of (VAc+AcrA) increases with increasing concentration of the organic phase. In systems with the nonreactive cosurfactants ethanol and propanol, the conversions of mixtures with VAc/SCC = 10/90 decrease with increasing o/w ratio [19, 20]. The presence of AcrA, whose reactivity with respect to VAc is higher [21], modifies the overall reactivity of the system (Fig. 5b, c-II). In initially homogeneous systems with high VAc content (Fig. 5c-I) the conversion also increases with increasing organic phase concentration. Unlike these systems, the conversion in the presence of nonreactive cosurfactants [19, 20] exhibits a minimum at a concentration close to the critical concentration of SCC with respect to water.

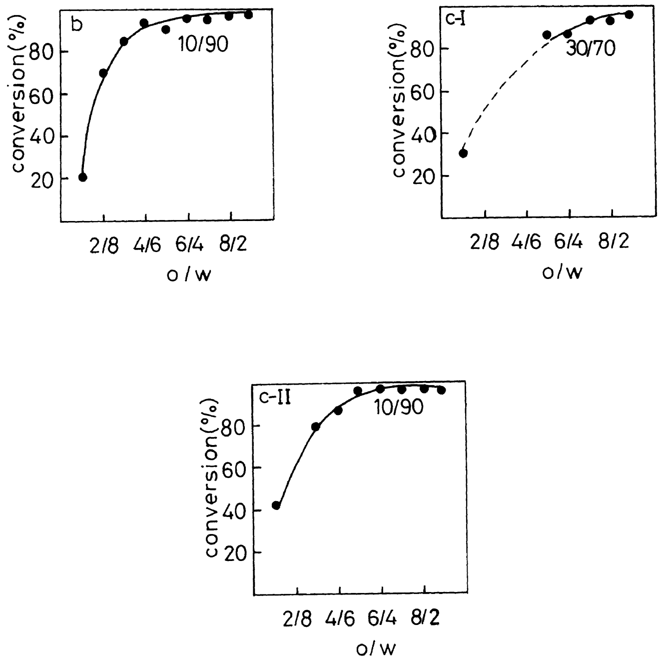

Fig. 5 The dependence of conversion on o/w ratio for the homogeneous systems shown in Fig. 1b, c [24 h; 65 °C; VAc/AcrA = 10/90 (*b, c-II*), 30/70 (*cI*)]

The maleic group of the crosslinked monomer (MDEGM) lowers the final conversion of the system at a low o/w ratio (Fig. 5b, c-II). At higher concentrations of the organic phase the final conversions have similar values in the presence or the absence of MEDGM.

When crosslinked polymers obtained in the presence of MDEGM are immersed in water, they absorb water and become gels. The dependence of the water content of some gels on the synthesis conditions is shown in Fig. 6.

At the same content of crosslinked monomer the water absorbed decreases with increasing VAc concentration. Poly(VAc), unlike poly(AcrA), swells in water [22]. It is therefore normal that, in good agreement with other results [23], the presence of some less polar structural units, for example VAc, determines the decrease in water absorption.

The amount of water absorbed by VAc/AcrA gels decreases, by the same ratio of the comonomers, with the decreasing by the initial ratio of aqueous phase (o/w is 7/3 with respect to 9/1). In initially homogeneous systems whose w/o structure is bicontinuous, water plays the role of an inactive diluent [1, 4]. Owing to the initial nanostructuring, the aqueous zones determine the increase in interchain separation of the hydrophobic zone that contains the monomers. Following crosslinking, the polymers with a higher aqueous phase content spread more extensively, finally allowing a greater amount of water to penetrate the network inner cell domains. The absorption of water also increases owing to the increase of poly(ethylene oxide) groups in the copolymerized surfactant whose concentration in the polymer increases with that of aqueous phase.

The decrease in the amount of absorbed water also occurs following the increase in the MDEGM crosslinked monomer concentration (Fig. 6). This is a law already established in crosslinked polymers [24]. The decreasing of polymer network size normally lowers the amount of water that can be accepted.

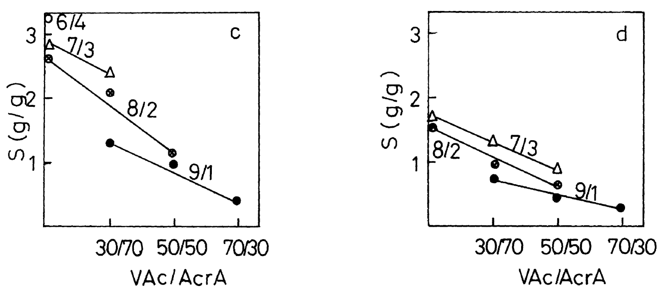

Fig. 6 Water absorption of gels resulting from polymerization of homogeneous systems versus VAc/AcrA [o/w = 9/1, 8/2, 7/3, 6/4; bis maleate diethylene glycol (MDEGM) monomer = 5% (*c*), 10% (*d*); 96 h]

It was proved that during polymerization of similar systems [1, 2, 4], the formation of polymer networks is accompanied by phase separations and the coalescence of aqueous zones. The dimensions of the pores in the polymer formed are higher than those of the microdomains from initial microemulsions.

The morphology of the polymers depends on the initial composition of the microemulsions. Electron microscopy and the monitoring of water desorption from swollen networks have revealed network structures with closed pores corresponding to initial w/o microemulsions. The increase in water content in the precursor microemulsions generates a transition from closed pores to porous structures with open pores corresponding to bicontinuous structures [1, 2, 4].

The study of water absorption carried out in this contribution has revealed distinctions which originate in the initial composition of microemulsions (Fig. 6). In the case of hydrogels, the absorption can be analyzed by means of the equation

$$M_t/M = K_1 t^{0.5} \quad , \tag{4}$$

where M_t and M are the amount of water absorbed at time t and at equilibrium, respectively, and K_1 is a constant that depends on the network inner cell domains. The 0.5 exponent shows that the first step in the water absorption process takes place according to a mechanism proposed by Fick [26].

Information relating to the kinetics of swelling can be obtained by making use of the following equation [27]:

$$S_t = K_2 t^{0.5} \quad , \tag{5}$$

where S_t is the degree of swelling at time t and K_2 is the swelling rate coefficient.

K_2 is calculated from the slope of the linear phase which represents $S_t = f(t^{0.5})$: its value depends of the polymer network.

A first study on swelling phenomenon was carried out on poly(AcrA) gels (Fig. 7). The degree of swelling is analyzed as a function of the H_2O/AcrA ratio in the initial polymerized mixtures (Fig. 7 line a).

The dry gels swell with water to an extent which depends on the morphology of the networks formed by polymerization [1, 2, 4]. The critical concentration of 1 mole AcrA/5 mol H_2O is marked in Fig. 7 at H_2O/AcrA = 1.27. At lower values bicontinuous structures and w/o structures are formed with strong bonds between the polymeric domains. Above this value, the network is much looser: the pores initially open are probably modified owing to the weak consistency of the polymer network. Therefore in the region of AcrA critical concentration the degree of swelling changes.

Another significant jump within this domain is undergone by K_2, the swelling rate coefficient (Fig. 7 line c). The jump at H_2O/AcrA values higher than 1.27 is limited by the increase in water concentration caused by the looseness of the polymer network. The increase in K_2 points to an increase in swelling rate which accompanies the extension of the aqueous phase microdomains from the networks formed, in good agreement with the results in Fig. 6; the modification of this coefficient occurs at a H_2O/AcrA ratio lower than 0.25, a value which corresponds to some initial structures of w/o-type (Fig. 1).

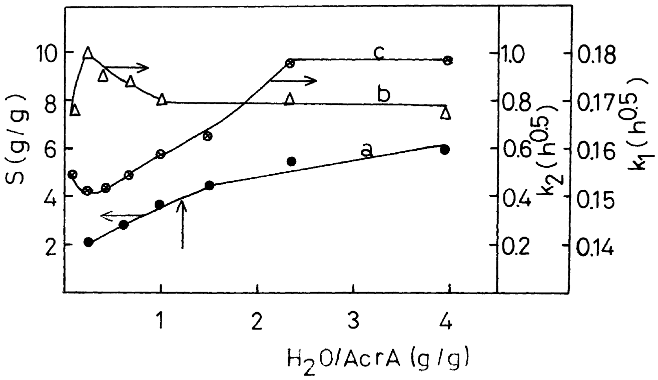

Fig. 7 The dependence of the degree of swelling S (*a*) of poly(AcrA) and of K_1 (*b*) and K_2 (*c*) on H_2O/AcrA (MDEGM/AcrA = 10%; see Eqs. 4, 5 for definitions of K_1, K_2)

The constant K_1 in Eq. (4) (Fig. 7 line c) also undergoes suggestive changes. The values obtained suggest the modification of the polymer network in three distinct zones of H_2O/AcrA ratio:

I. H_2O/AcrA < 0.25 corresponding to the w/o initial structures;
II. H_2O/AcrA ∈ [0.25–1.27] corresponding to bicontinuous-type initial structures;
III. H_2O/AcrA > 1.27 corresponding to initial o/w structures.

The results presented so far represent additional arguments which support the idea that the structure of microporous polymers obtained by polymerization in microemulsions in the presence of SCC depends on the structure of the initial systems [1, 2, 4].

The analysis of K_1 and K_2 in conditions of VAc-AcrA copolymerization (Fig. 6) is more difficult to carry out because homogeneous gels were obtained over a narrow o/w (9/1–6/4) interval. The data in Fig. 1 suggest that over the range of initial w/o structures bicontinuous gels were also obtained. The experimental data suggest that the value of the swelling coefficient, K_2, increases with increasing aqueous phase and AcrA concentration in the monomer mixture. The opposite effect occurs for K_1: its value increases with decreasing aqueous phase and AcrA concentration. Within the limits of the composition range mentioned the results agree with those in Fig. 7 (lines b, c)

One can conclude that AcrA is a short-chain cosurfactant, efficient in production of homogeneous systems formed in the presence of vinyl acetate and water with or without surfactant. The nonlinear modification of the refractive indexes and the conductivity of homogeneous systems, when water concentration increases, proves that the nanostructuring evidenced in AcrA/H_2O solutions is preserved.

Microemulsions of w/o, bicontinuous, and o/w structures are formed. The final conversion of the systems studied increases with increasing organic phase concentration, a behavior unlike that of the systems containing nonreactive SCC. The water absorption of the final gels obtained in the presence of a crosslinked monomer decreases with increasing concentrations of the monomer, of vinyl acetate and the organic phase in the initial systems.

References

1. Palani Raj WR, Sasthav M, Cheung HM (1993) J Appl Polym Sci 47:499
2. Palani Raj WR, Sasthav M, Cheung HM (1991) Langmuir 7:2586
3. Chew CH, Gan LM (1985) J Polym Sci Polym Chem Ed 23:2225
4. Palani Raj WR, Sasthav M, Cheung HM (1995) Polymer 36:2637
5. Smith GH, Donelan CE, Barden RE (1977) J Colloid Interface Sci 60:488
6. Borys NF, Holt SL, Barden RE (1979) J Colloid Interface Sci 71:526
7. Keiser BA, Varie D, Barden RE, Holt SL (1979) J Phys Chem 83:1276
8. Keiser BA, Holt SL, Barden RE (1980) J Colloid Interface Sci 73:290
9. Barden RE, Holt SL (1984) In: Mittal KL, Lindman B (eds) Surfactants in solution vol 2. Plenum, New York, p 707
10. Kunz W, Fries PH, Turq P (1995) J Chim Phys 92:601
11. Fries PH, Kunz W, Turq P (1995) J Chim Phys 92:614
12. Grossman GH, Ebert KH (1981) Ber Bunsenges Phys Chem 85:1026
13. Mashimo S, Umehara T, Redlin H (1991) J Chem Phys 95:6257
14. Mashimo S, Miura N, Umehara T (1992) J Chem Phys 97:6759
15. Kronberg B, Costas M, Silverston R (1994) J Dispersion Sci Technol 15:333
16. Langevin D (1992) Annu Rev Phys Chem 43:341
17. Olson U, Wennrström H (1994) Adv Colloid Interface Sci 49:113
18. Donescu D, Fusulan L, Petcu C (1997) Colloid Polym Sci 275:903
19. Donescu D, Fusulan L (1994) Synth Polym J 1:241
20. Donescu D, Fusulan L, Gosa K (1997) J Macromol Sci Pure Appl Chem A34:675
21. Mark H, Immergut B, Immergutin EH, Brandrup J, Immergut EH (eds) (1966) Polymer Handbook, Int Pube, II-143
22. Donescu D, Ciupitoiu A, Gosa K, Languri J (1993) Rev Roum Chim 38:1441
23. Takigami S, Kimura T, Makamura Y (1993) Polymer 24:604
24. Allen PEM, Bennett DJ, Williams DS (1993) Eur Polym J 29:231
25. Gehrke SH (1993) In: Durek K (ed) Responsive gels vol II. Springer, Berlin Heidelberg New York p 81
26. Peppas N, Fronson N (1981) J Polym Sci Polym Phys Ed 21:983
27. Urushizaki F, Yamaguchi H, Nakamura K, Numajiri S, Sugibayashi K, Morimoto Y (1990) Int J Pharm 58:135