

Dispersions of Polymeric Acrylic Soaps I— The Relationship between the Hydrophilic/ Hydrophobic Balance and the Dispersibility of the Polymers

N. B. GRAHAM* and H. W. HOLDEN

The preparation of dispersions of partially to completely neutralized, low-molecular-weight acrylic and methacrylic acid copolymers is described. Over a particular range of hydrophilic/hydrophobic balance in the molecules, stable dispersions are very readily formed. The maximum practical polymer content of the dispersion can be markedly greater with partial neutralization than with complete neutralization.

Low molecular weight anionic soaps have been important items of commerce and everyday life for many thousands of years. Soaps are typified by a number of characteristics, amongst which low solubility in water, the ability to form micelles at higher concentrations and to emulsify water-insoluble materials are some of the more important. Effective soaps have a ratio of hydrophilic to hydrophobic groups within certain rather broad limits. Thus, the sodium salts of low molecular weight acids such as acetic, propionic and butyric are not effective as soaps, whereas sodium stearate with eighteen carbon atoms is effective.

Polymeric anionic soaps present a unique, and relatively uninvestigated, class of materials in which the size of the molecule and the ratio of hydrophilic to hydrophobic portions can be varied at will by copolymerization. It is also possible to copolymerize various complexing groups into the polymer and to study such effects as hydrogen bonding on the soap properties.

This paper describes the preparation of a series of polymeric soaps, attempts to define the hydrophilic/hydrophobic balance required for these materials to be effective and shows how they give stable emulsions; some of these polymers may be self-emulsifiable and may give thermodynamically stable micelles. The use of these polymeric soaps in emulsification of other water-insoluble organic compounds and polymers is briefly described.

EXPERIMENTAL

Preparation of copolymers

The commercial monomers were usually used without additional purification. In a typical polymerization, a 500g quantity of mixed monomers containing 10g of benzoyl peroxide was added over a period of two hours to 250g of stirred refluxing isopropanol; the mixture was then refluxed for

*Present address: I.C.I. Ltd, Petrochemical and Polymer Laboratory, P.O. Box 11, The Heath, Runcorn, Cheshire, England.

Table 1. Copolymers and their water dilution values. Nominal composition (weight percentage of monomer)

| Number | Vinyl toluene | Styrene | 2-Ethylhexyl acrylate | Butyl methacrylate | Butyl acrylate | Ethyl acrylate | Methyl methacrylate | Methyl acrylate | Methacrylic acid | Acrylic acid | Acrylamide | N-methylolacrylamide | Water Dilution Value |
|--------|---------------|---------|-----------------------|--------------------|----------------|----------------|---------------------|-----------------|------------------|--------------|------------|----------------------|----------------------|
| | VT | S | 2EHA | BMA | BA | EA | MMA | MA | MAA | AA | AAm | NMAAm | |
| 1 | | | | | | | | 80 | | 20 | | | 989 |
| 2 | | 25 | | | | | | | | 75 | | | 924 |
| 3 | | | | | | 80 | | | | 20 | | | 557 |
| 4 | | | | | | 88 | | | | 12 | | | 552 |
| 5 | | | | | | | 80 | | 20 | | | | 567 |
| 6 | | | | | | | | 95 | | 5 | | | 443 |
| 7 | | | | | | | 88 | | 12 | | | | 424 |
| 8 | | | | | | | | | | 5 | | | 278 |
| 9 | | 10 | | | | 75 | 95 | | | 4 | | 11 | 278 |
| 10 | | | | | | | 95 | | 5 | | | | 272 |
| 11 | | | | | | 40 | 50 | | | 3 | 7 | | 265 |
| 12 | | | 39 | | | | 50 | | | 5 | | 6 | 235 |
| 13 | | | | | 90 | | | | | 10 | | | 227 |
| 14 | | 22 | | | | 53·6 | 9·4 | | | 15 | | | 177 |
| 15 | | 10 | | | | 5 | 20 | | | 15 | | | 172 |
| 16 | | 40 | 50 | | | 40 | | | | 20 | | | 166 |
| 17 | | 22 | | | | 53·6 | 9·4 | | | 12 | 3 | | 165 |
| 18 | | 22 | | | | 53·6 | 9·4 | | | 6 | 9 | | 164 |
| 19 | | 22 | | | | 53·6 | 9·4 | | | 4 | 11 | | 157 |
| 20 | | 10 | | | | | 25 | | | 5 | | 7 | 127 |
| 21 | | 22 | 53 | | | 53·6 | 9·4 | | | 9 | 6 | | 127 |
| 22 | | 58 | | | | | 20 | | | 5 | | 7 | 105 |
| 23 | | 10 | | | | 63 | 15 | | | 5 | | 7 | 90 |
| 24 | | 20 | 65 | | | | | | | 4 | | 11 | 82 |
| 25 | | 15 | 73 | | | | | | | 4 | | 8 | 68 |
| 26 | | 15 | 73 | | | | | | | 5 | | 7 | 68 |
| 27 | 66 | | | | | 20 | | | | 14 | | | 68 |
| 28 | | 10 | 78 | | | | | | | 5 | | 7 | 56 |
| 29 | | 5 | 83 | | | | | | | 5 | | 7 | 55 |
| 30 | | 47·5 | | | | 47·5 | | | | 5 | | | 50 |
| 31 | | | | | 50 | | | | | 50 | | | |
| 32 | | | | | 70 | | | | | 30 | | | |
| 33 | | | | | 97 | | | | | 3 | | | |
| 34 | | 15 | | 70 | | | | | | 5 | 10 | | |
| 35 | | 10 | 55 | | | | 20 | | | 11 | 4 | | |
| 36 | | 70 | | | | 15 | | | | 6 | 9 | | |
| 37 | | 45 | | | | 45 | | | | 10 | | | |

a further four hours at which time the conversion to polymer was shown to be 96 to 99·8 per cent complete. Some of the isopropanol was then distilled off and polymer content adjusted to various levels for subsequent experiments. Table 1 gives a list of polymers prepared by this or similar procedures.

The following empirical test was devised as a simple means of measuring the hydrophilic character of the polymers. At room temperature, a weighed sample of the polymer solution was adjusted to 40 per cent polymer by addition of isopropanol, then diluted to ten per cent polymer with 2-ethoxy-ethanol. The solution was titrated with distilled water until a permanent haze formed; the titre in ml/100g of polymer is defined as the Water Dilution Value (WDV).

Preparation of aqueous copolymer dispersions

The isopropanol solution of copolymer from the foregoing preparation was concentrated to the range 75 to 90 per cent polymer by distillation of solvent using steam heating. The mixture was then cooled to 50°C, the calculated amount of base for partial neutralization of the copolymerized acid was added, and stirring continued for 20 minutes. The temperature was increased again to 90°C and heated distilled water was added over 30 to 60 minutes with as rapid stirring as possible. In cases where emulsions formed, the first water added gave thick viscous mixtures, presumably with the water dispersed in the polymeric phase. Further addition led gradually, or from time to time suddenly, to a thin blue-white polymer-in-water emulsion.

The occasional use of a more lengthy procedure of emulsification led to some extremely stable emulsions; the steps involved were: (i) removal under vacuum of virtually all the isopropanol from the polymer, (ii) addition of the calculated amount of base and water all together and (iii) vigorous stirring of the solution above the viscous polymer with heat applied if necessary. In the early stages, a portion of the polymer appeared to dissolve outright and the solution became very frothy. After some time the top layer of the clear remaining polymer swelled and whitened and was swept away by the stirring action; foaming diminished, the liquid became opaque and eventually all the polymer was emulsified.

Emulsification with polymeric soaps

Isopropanol-free dispersions of copolymer 35 (Table I) were prepared at 0.69 and 1.00 neutralization with triethylamine. Various proportions of polymer, water and selected organic liquid were mixed for five minutes in a Waring blender, and the resulting dispersion was examined for stability after standing 24 hours.

Particle size determination

The emulsions were diluted with a suitable quantity of distilled water, and photographed with the aid of a Vickers projection microscope. Usually, oil immersion phase-contrast optics was used to obtain a magnification of 2000×. The particle sizes could be measured directly when greater than 0.5 micron. Smaller particles although visually distinguishable could not be photographed because of Brownian motion.

Copolymer for molecular weight determination

A copolymer was made by reacting styrene, acrylic acid and benzoyl

peroxide (weight ratio 75-25-1) in isopropanol solution. All the constituents were added to the reaction vessel at the start of the polymerization. After 13 per cent conversion, the product was precipitated by pouring the mixture into methanol; the solids were then taken up in acetone and reprecipitated with water. The dried polymer contained 19.6 per cent by weight of acrylic acid, as shown by titration with sodium hydroxide. A sample was completely methylated using diazomethane in acetone, precipitated again and dried in vacuum at 50°C. The number average molecular weight of this preparation, as determined in chloroform solution with a Mechrolab 302 vapour pressure osmometer, was $8\,200 \pm 800$.

RESULTS

Figure 1 summarizes the dispersibility behaviour in water of a number of butyl acrylate-acrylic acid copolymers (13, 31, 32, 33 of *Table 1*). For these illustrative experiments, solutions of 80 per cent polymer in isopropanol were prepared. A calculated amount of aqueous ten per cent sodium hydroxide solution was added and thoroughly mixed. The percentage of polymer in these partially neutralized solutions is shown in *Figure 1 (a)*.

Sometimes the addition of the relatively small amount of water with the base was sufficient to cause phase separation, as indicated by the solid symbols in *Figure 1 (a)*. In other cases the amount of additional water required to produce phase separation was recorded as shown in *Figure 1 (b)*. The points on the axis 'zero % neutralization' were obtained from the cloud end points of titration of the polymer solutions, without added sodium hydroxide, against water. It may be seen that the polymers containing 30 and 50 per cent acrylic acid became completely miscible with water when only partially neutralized; however, the miscibility of water in polymers containing ten per cent and three per cent acid, as deduced from *Figure 1 (a)*, is low at all levels of neutralization.

The addition of water was continued with stirring. In all cases with the 97-3 copolymer, and at low levels of neutralization with the other copolymers, the systems remained as inhomogeneous slurries. In certain cases the stirred mixture appeared as a white viscous phase with the excess added water becoming incorporated rather slowly into it. At some fairly critical and reproducible composition, the system became a homogeneous dispersion with a significant reduction in viscosity. Such occurrences are observed in emulsion systems as the result of phase inversion or of reduction in partial volume of the disperse phase below a critical packing value⁹.

The compositions of the systems at this critical stage are shown in *Figure 1 (c)*. The 90-10 copolymer gave dispersions over a broad range of neutralization values with relative ease; those produced at about 50 per cent neutralization were emulsions with particles less than one micron in diameter. Because of high solubility at higher levels of neutralization the 70-30 and 50-50 copolymers were capable of forming emulsions only in a narrow range of neutralization. Only two examples of emulsions of the former, and one rather unstable dispersion of the latter were prepared.

The best emulsions of the 90-10 copolymer were stable at a higher polymer content than that obtainable for the fully neutralized copolymer.

DISPERSIONS OF POLYMERIC ACRYLIC SOAPS I

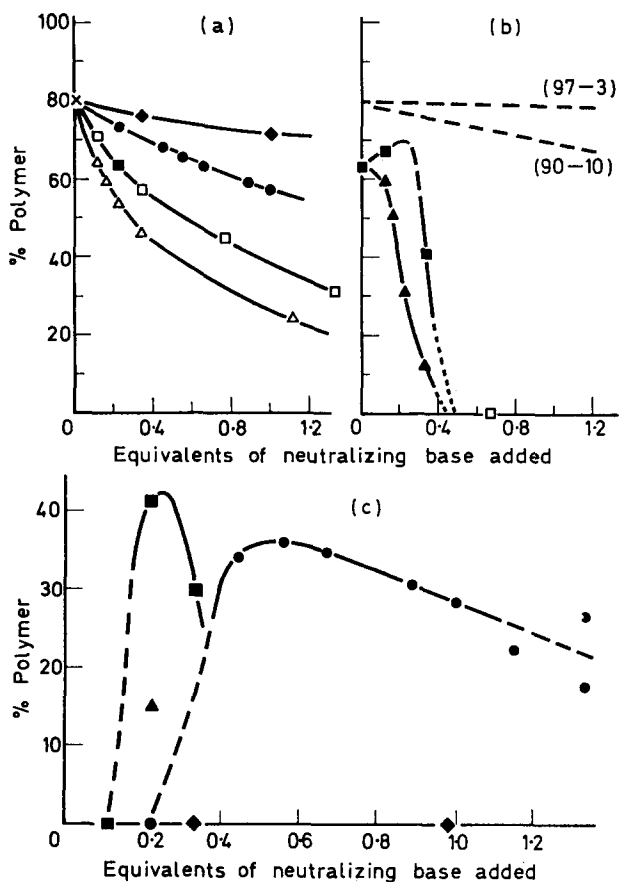


Figure 1—Demonstration of behaviour of butyl acrylate-acrylic acid copolymer systems at successive stages of the neutralization and dispersion procedure.

- (a) Weight per cent polymer in systems after addition of aqueous base, at beginning of water addition. ×: all copolymers, no base added; △ ▲: 50-50 copolymer; □ ■: 70-30 copolymer; ○ ●: 90-10 copolymer; ◇ ◆: 97-3 copolymer. Open symbols represent homogeneous systems; solid symbols two-phase systems
- (b) Weight per cent polymer in systems when separation into two phases first observed. Dashed curves are postulated relations (where phase separation occurred before start of water addition). Same symbols as in (a).
- (c) Weight per cent polymer in systems at first formation of low-viscosity dispersions. Same symbols as in (a).

The dispersions became more transparent as the level of neutralizing base was increased from 0.44 to 1.33 equivalents.

As a general rule it was found that more hydrophobic copolymers showed lower 'solubility' when fully neutralized, but produced stable emulsions of the highest polymer content. This behaviour correlates with

the Water Dilution Values given in *Table 1*. Polymers 1 to 7 (WDV > 400) showed no signs of emulsification; 8 to 13 (WDV between 200 and 300) gave stable emulsions only below 35 per cent polymer content; 14 to 20 (WDV between 100 and 200) gave stable emulsions of up to 50 per cent polymer content; 23 to 30 (WDV < 100) would not emulsify. The word solubility as used here is merely an indication of a transparent system. It was impossible from visual or microscopic examination to tell whether the fully neutralized polymer preparations represented ultrafine emulsions or true solutions. Since they were still hazy and scattered light in a characteristic manner, they probably contained aggregates of greater than monomolecular size.

While the WDV is not an additive property of the monomers, it may be seen from *Table 1* that their effectiveness in altering the WDV may be ranked in the approximate order NMAAm > MAA > AAm > AA > MA > MMA \approx EA > BA > BMA > 2EHA > S > VT. The substitution of one monomer by a less hydrophilic one always lowered the WDV; this result suggests a number of other hydrocarbon types which could be used to lower the WDV into the preferred range.

Effect of acid level

The only two monomer acids studied appeared roughly equivalent in emulsifying power. No stable emulsions were formed from copolymers containing less than four per cent by weight of acrylic acid. The most stable ones (as measured by the amount of sodium chloride solution required to cause coagulation) were formed with copolymers containing ten per cent or more by weight of acrylic acid.

The effect of various bases and degrees of neutralization

A study was made using three styrene-ethyl acrylate-acrylic acid copolymers designated by 16, 30 and 37 in *Table 1*. In these experiments all dispersions were reduced to the relatively low level of 21 to 25 per cent polymer in order to compare relative stability on storage.

Table 2 gives some of the details of emulsions made using sodium hydroxide or ammonia with the 40-40-20 copolymer. The most stable sodium hydroxide emulsion, containing the smallest particles, occurred at 60 per cent neutralization; for ammonia, the optimum level was 70 per cent and the emulsion was much less stable. The term settling, as used in the table, signifies the sedimentation of large particles where the influence of gravity is large compared to Brownian motion; while coalescence of particles undoubtedly occurs, such systems can be readily redispersed with little agitation. On the other hand coagulation can be detected microscopically at a very early stage by the occurrence of large aggregates of particles which eventually coalesce as a distinct, separate phase.

With systematic variation of the level of neutralization, it is often difficult to characterize systems neutralized beyond the optimum amount. The opacity can diminish greatly while the viscosity can increase markedly. The decrease in opacity could be caused by either the dissolution of the polymer or by a marked reduction in particle size. The increase in vis-

Table 2. Emulsification behaviour of copolymer no. 16 (S40-EA40-AA20) at various levels of neutralization

| Degree of neutralization | Base sodium hydroxide | | Base ammonia | |
|--------------------------|-----------------------|---|-------------------|---|
| | Dispersion* | Stability | Dispersion* | Stability |
| 0.1 | None | | Not tested | |
| 0.2 | 1-4 | Settled slightly after 18 h and completely after 10 months | Coarse | Nearly complete settling after 18 h |
| 0.3 | 1-2.5 | " | Coarse | Nearly complete settling after 18 h |
| 0.4 | 0.5-1.5 | " | Coarse | Slight settling after 18 h |
| 0.5 | 0.5-1 | Considerable settling at 10 mos | Coarse | Slight settling after 18 h |
| 0.6 | <0.5 | No settling after 10 mos | <10 | Slight settling after 18 h. Nearly complete settling after 10 mos |
| 0.7 | 0.5-2 | Particles present as agglomerates | Few ~6, mostly <1 | Considerable settling after 10 mos |
| 0.8 | Thick | Heavy coagulation in a few weeks | Coarse | Coagulated overnight |
| 0.9 | Viscous | Separation observable after two days | Coarse | Coagulated overnight |
| 1.0 | Hazy | Two phases separated in 18 h; became one with addition of water | Milky | Two phases separated in 18 h. Saturated 'solution' contained 5.1% polymer |

*Particle size in microns.

cosity could be caused by the dissolution of the polymer or by an increase in the phase volume occupied by the disperse phase. These points will be discussed in later papers.

In *Table 3* the performance of a number of bases is summarized; complex contributing factors are indicated. As a result of these and other experiments, it was found as a general rule that ammonia and the primary amines were poor emulsifiers which nevertheless gave some good emulsions with polymers containing 10 to 20 per cent acid. On the other hand secondary and tertiary amines and sodium hydroxide were effective as emulsifiers and gave good emulsions with some polymers containing as little as four per cent acid. The optimum amount of base was usually readily defined, as indicated in *Table 2* (i.e. within about ± 5 per cent of neutralization of the polymer acid); the optimum is also seen to vary somewhat with the choice of base. In addition it was noted that copolymers having compositions favouring higher water dilution values (see examples in *Table 3*) produced their best emulsions at a lower fractional neutralization.

Table 3. Degree of neutralization, maximum particle size and stability of optimum emulsion compositions observed for S-EA-AA copolymers of indicated monomer wt ratios

| Neutralizing bases | 40-40-20 | 45-45-10 | 47.5-47.5-5 |
|--|--------------------|---------------------|-------------|
| NaOH | 60%, 0.5 μ , v | | |
| NH ₃ | 70%, 1 μ , m | 30-80%, u | 70-100%, u |
| N(CH ₂ CH ₂ OH) ₃ | 60%, 1 μ , m | 100%, 0.3 μ , f | 60-100%, u |
| N(CH ₃) ₃ | 65%, 0.3 μ , v | | |
| N(C ₂ H ₅) ₃ | 70%, 0.3 μ , v | 80%, 0.3 μ , v | 100%, f |
| C ₂ H ₅ NH ₂ | 80%, 0.3 μ , v | | |
| (C ₂ H ₅) ₂ NH | 70%, 0.5 μ , m | | |
| (n-C ₃ H ₇)NH ₂ | 60%, —, f | | |
| (n-C ₄ H ₉) ₂ NH | Would not emulsify | | |

v very stable: no separation after 10 months.

m moderately stable: slight separation after 10 months.

f fairly stable: considerable separation after 10 months.

u unstable: considerable separation in two weeks.

Self-dispersed polymers as emulsifiers

The emulsions were capable of carrying inert materials into suspension. Thus six parts of an emulsion of copolymer 34 of *Table 1* would emulsify 94 parts of ethyl acetate merely by shaking the dilute emulsion with the ethyl acetate in a test tube. This copolymer was equally effective as an emulsifier for methyl methacrylate but very much less effective for styrene or benzene. Water-insoluble resins such as urea-formaldehyde resins or epoxy resins have also been emulsified by these self-dispersed polymer emulsions. Some results for copolymer 35 are given in *Table 4* for emulsions which were rated after standing for 24 hours.

The particles of emulsions with a rating of one in the above table were so small that they could not be seen by phase contrast microscopy using a magnification of 2 000 \times .

Stability of the emulsions

Many emulsions were stored for as long as eighteen months without noticeable change or settling. When already nine months old, an ammonia-

Table 4. Survey of characteristics of copolymer 35 (Table 1) as an emulsifying agent

| Ratio organic liquid/polymer (by weight) | Solubility parameter (cal/cm ³) ^{1/2} : | | Ethyl-ene chlor-ide | | Cyclo- Methyl- hexa- metha- Decene | | I- Decene | | N- Decane | | | | | |
|--|--|---------------------------------|---------------------|-----------------------|--|--------------------|--|-----------------------|---------------------|--------------------|------|-----|------|------|
| | Percentage of organic liquid and polymer | Percentage of water (by weight) | Aceto- phe- none | Ethyl- ene chlor- ide | 100% neutralization | 69% neutralization | Aceto- phe- none | Ethyl- ene chlor- ide | 100% neutralization | 69% neutralization | | | | |
| 1:1 | 24.9 | 75.1 | 10.43 | 9.96 | 9.26 | 8.8 | 7.90 | 7.77 | 10.43 | 9.96 | 9.26 | 8.8 | 7.90 | 7.77 |
| 2:1 | 33.2 | 66.8 | H3 | H1 | H3 | H1 | S4 | S4 | H2 | S4 | H3 | H1 | S4 | S4 |
| 2.82:1 | 38.7 | 61.3 | H4 | H2 | H3 | H2 | S4 | S4 | S4 | S4 | H4 | S4 | S4 | S4 |
| 5.65:1 | 52.3 | 47.7 | H4, C | S4 | S4 | S2 | S4 | S4 | S4 | S4 | S4 | S4 | S4 | S4 |
| 6.54:1 | 56.9 | 43.1 | H4 | C | On dilution to 28.5% this became fluid and homogeneous | | On dilution to 32.1% this became fluid but separated overnight | | S4 | S4 | S4 | S4 | S4 | S4 |
| 7.06:1 | 60.4 | 39.6 | C | C | On dilution to 32.1% this became fluid but separated overnight | | On dilution to 32.1% this became fluid but separated overnight | | H3 | H1 | H4 | H1 | S4 | S4 |
| 1:1 | 12.4 | 87.6 | H3 | H1 | H4 | H1 | S4 | S4 | H2 | S4 | H4 | H2 | S4 | S4 |
| 2:1 | 16.6 | 93.4 | H4 | H2 | H4 | H2 | S4 | S4 | H4 | H4 | S4 | H4 | S4 | S4 |
| 2.82:1 | 19.4 | 80.6 | H4 | H4 | H4 | H4 | S4 | S4 | S4 | S4 | S4 | S4 | S4 | S1 |
| 5.65:1 | 26.9 | 73.1 | H4 | H4 | S4 | S4 | S4 | S1 | H2 | S4 | H4 | H4 | S4 | S1 |

Legend (1) Apparently clear solution showing Tyndall effect.

(2) Apparently clear solution showing very marked Tyndall effect.

(3) Blue-white emulsion.

(4) White emulsion.

S=separation

H=homogeneous

C=cream.

neutralized emulsion of styrene-ethyl acrylate-acrylic acid-acrylamide 20-60-17-3 was put through eighteen freeze/thaw cycles but no change in particle size or viscosity was observed. An emulsion of styrene-ethyl acrylate-acrylic acid 20-60-20 which had been made using ammonia and stored for six months, showed no significant change in properties from those observed initially.

The stability of the emulsions to added salts

No beneficial effect was noticed when emulsifications of the above copolymer were attempted using sodium chloride solution from 0.005 to 0.1 molar instead of distilled water. The emulsions could not be prepared in sodium chloride solutions more concentrated than 0.07 molar.

DISCUSSION

A number of relevant papers on the use of homopolymers and copolymers of acrylic and methacrylic acids (for example refs. 1-8) have appeared in the last two decades. These previous papers dealt with the viscosities and ionization of high molecular weight polymers and also briefly with the ability of polymethacrylic acid to solubilize hydrocarbons⁶. The studies reported in this and subsequent papers are different from previous work in that they deal with comparatively low molecular weight polymers (\bar{M}_n of approximately 5 000 to 20 000). Some of these copolymers have rather unusual compositions, having been made for a programme of industrial research which need not concern us here. The complexity of the copolymers does not affect their use as examples of polymeric soaps.

The polymers appeared to fit into four broad overlapping classes typified by the examples shown in *Figure 1*: (a) completely soluble in water without neutralization; (b) completely soluble in water in all proportions when fully neutralized; (c) not very soluble in water when fully neutralized but readily

Table 5. A comparison of Water Dilution Value (WDV), solubility parameter (δ), H-bonding number (γ) and dipole moment (μ) for mixtures of isopropanol, 2-ethoxyethanol and water (units of γ are defined in paper by Crowley *et al.*¹⁰)

| WDV | δ (cal/cm ³) ^{1/2} | μ (Debye units) | γ |
|-----|---|------------------------|----------|
| 50 | 10.8 | . | 15.3 |
| 100 | 11.4 | . | 16.4 |
| | | Nearly | |
| 150 | 11.9 | . | 17.3 |
| 200 | 12.4 | . | 18.2 |
| | | constant | |
| 250 | 12.9 | . | 19.1 |
| 300 | 13.3 | . | 19.8 |
| 350 | 13.7 | . | 20.6 |
| 400 | 14.0 | . | 21.2 |

These figures have been calculated using the following values for the pure components:

| | δ | μ | γ | Density (g/cm ³) |
|-----------------|----------|-------|----------|---------------------------------|
| Isopropanol | 11.5 | 1.7 | 18.7 | 0.786 |
| 2-ethoxyethanol | 9.9 | 1.6 | 13.0 | 0.931 |
| Water | 23.5 | 1.8 | 39.0 | 0.999 |

dispersed to a stable emulsion of high polymer content when partially neutralized; (d) insoluble in water and not dispersible in water in either the neutralized or acidic forms.

This unusual behaviour of class (c) polymers appears to be general for materials within a particular range of the hydrophilic/hydrophobic balance, characterized in *Table 1* by WDV of 100 to 400 and exemplified in detail for copolymer 16 in *Table 2*. The variation in emulsification with base is not surprising, as it is well known⁴ that the strength of polymeric acid varies with the nature of the base being used for its neutralization. In passing it is worth commenting that the very empirical WDV can be correlated with the solubility parameters and H-bonding number γ of the isopropanol-water-2-ethoxyethanol mixtures according to the method of Crowley *et al.*¹⁰ (*Table 5*).

The dispersion phenomenon is shown more clearly in *Figure 2*, which is largely self-explanatory. This diagram is more typical of the rather more hydrophobic copolymers with water dilution values from 100 to 200. The division between the compositions giving unstable and stable dispersions is drawn as a zone to indicate that it is not sharp and varies to some extent with the temperature and the emulsification conditions. *Figure 2* is not an experimentally obtained curve but rather a generalization from the many results obtained in this work.

These class (c) polymers are effective dispersing agents for solvents, monomers and other polymers. The effectiveness of the emulsifying agent varies with the nature of the material being emulsified. With a fully

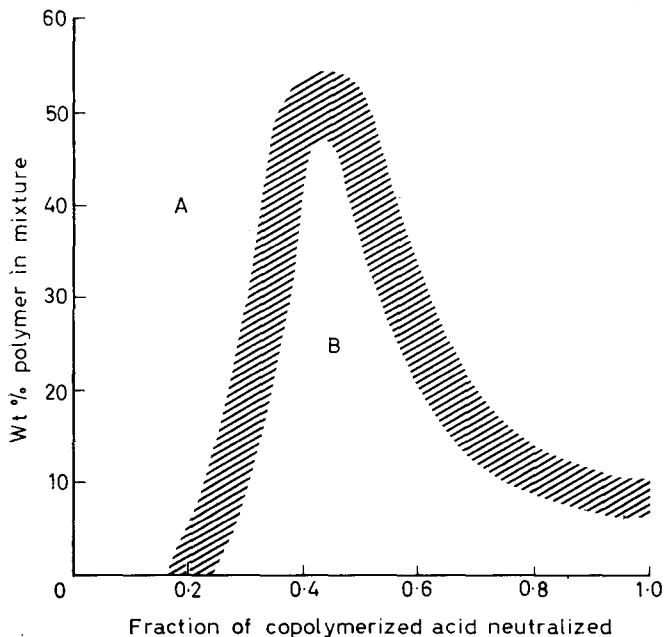


Figure 2—Typical dispersibility behaviour of acrylic acid copolymers in water. Region A: field of unstable dispersions; region B: field of stable dispersions; hatched area: transition region

neutralized emulsion, the stability and amount of organic liquid capable of emulsification increases with the solubility parameter of the solvent up to acetophenone (solubility parameter = 10.43). The partially neutralized polymer is a less efficient emulsifier and performs best with solvents of solubility parameter 9.0 to 9.96. The emulsions at above 52.33% w/w concentration or organic liquid/water are viscous creams; it is probable that some water is imbibed by the emulsion particles, and this increases the volume fraction of the disperse phase to a level where the particles are severely interfering with each other's movements.

CONCLUSIONS

A class of copolymers has been described which readily forms aqueous emulsions with very little agitation, to particles frequently less than 0.5 micron in diameter. Under certain circumstances these copolymers also emulsify liquids normally immiscible with water. A number of questions are raised by these results:

1. Are the dispersions the thermodynamically stable form of the polymer-base-water mixture perhaps analogous to the micelles formed with non-polymeric soaps?
2. Are the fully neutralized polymers in the form of a dispersion or are they a solution?
3. Why should dispersions of maximum polymer content be obtained with partially neutralized polymer?

These questions will be discussed in the subsequent papers.

The authors are pleased to acknowledge the experimental assistance of D. Pryshlakivsky, R. Veales and R. Auclair.

*Central Research Laboratory,
Canadian Industries Limited,
McMasterville, Quebec, Canada.*

(Received January 1969)

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