ON LINE CHARACTERISATION BY ACOUSTIC SPECTROSCOPY
OF "MODEL EMULSIONS" STABILISED BY POLY (VINYL ALCOHOL)

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The average droplet size and size distribution of 1-chlorobutane (ClBu)/water emulsions, as a model system of vinyl chloride (VCM)/water emulsions, were studied by acoustic spectroscopy on-line with an agitated laboratory reactor. The emulsions were stabilised with poly (vinyl alcohol-co-vinyl acetate) copolymers obtained by partial hydrolysis of poly (vinyl acetate). The effect of agitation speed, stirring time, concentration and hydrolysis degree of the copolymers, were investigated. A correlation between particle size and the ClBu/water interfacial tension could further be established.

INTRODUCTION

The industrial production of poly (vinyl chloride) (PVC) is essentially achieved by suspension polymerisation, a process where small droplets of vinyl chloride monomer (VCM), dispersed in an aqueous phase, are polymerised by free-radical initiation. The stability of the VCM/water emulsion is ensured by agitation and by the indispensable presence of so-called "protecting colloids", mainly vinyl alcohol-vinyl acetate copolymers (PVAs) obtained by the partial hydrolysis of poly (vinyl acetate) (PVAc). Thanks to their hydrophilic poly (vinyl alcohol) and hydrophobic poly (vinyl acetate) segments in the polymer chain, these copolymers, designated by PVA in the following, can adsorb at the VCM/water interface and provide the steric stabilisation of the VCM droplets.[1]

The molecular characteristics of PVAs, such as hydrolysis degree, molecular weight, length of acetate and alcohol segments and unsaturations have a very important influence on the stability of the VCM/water emulsion and on the properties of the final PVC resin.

For the optimisation of the polymerisation process, it is of interest to identify the factors governing the stabilisation of the initial VCM/water emulsions, keeping in mind that these emulsions, in a size range of 1 to 300 μm, are unstable in time and have a tendency to coalesce. Therefore it is important to control, not only the average droplet size, but also the size distribution of the droplets.

These characteristics have been studied for last decades by several authors who have determined the average drop size and size distribution by withdrawing samples from liquid-liquid dispersions prepared in agitated reactors and measuring them with microscopy techniques.[2-4] The main limitation of these techniques is that the emulsions have to be diluted and coalescence cannot always be avoided under static conditions, especially for relatively unstable emulsions of large droplet size.

For these reasons, the on-line monitoring of droplet's size has appeared to be the most appropriate technique. Chatzi *et al.*[5,6] have studied the effects of impeller speed, temperature and PVA concentration on styrene/water emulsions, with a styrene content of 1 vol%, by using an on-line laser diffraction technique. Recently, the in-situ real time measurements of droplet sizes and size distribution have been made possible by the development of new particle size analysers based on laser back scattering[7,8] or on ultrasonic attenuation spectroscopy.[9-12] This last granulometric technique has for instance been commercially developed by Sympatec under the trade name Opus. Based on the frequency dependent extinction of

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ultrasonic waves arising from droplets-waves interaction, Opus is advertised as to enable fast and sensitive on-line measurements of concentrated emulsions for particle size distributions from 1 μm to 3 mm.[11] In the present work, the Opus system was used to measure on-line the drop size distribution of 1-chlorobutane (ClBu)/water emulsions, as a model of VCM/water emulsions. The effects of agitation speed, stirring time, concentration and type of PVA were investigated and correlated to the ClBu/water interfacial tension in the presence of PVA.

RESULTS AND DISCUSSION

Influence of the agitation speed and stirring time on the ClBu droplet size and size distribution.

From the acoustic data determined separately for the emulsion and the aqueous phase as reference, one has access to the droplet size distribution and to the characteristics values D_{10}, D_{50} and D_{90} versus time. These values D_x mean that x vol% of the droplets have a mean diameter lower than D_x. The difference $(D_{90}-D_{10})$ is an indication of the polydispersity in droplet size of the emulsion.

A typical example is given in Figure 1, showing the evolution of the droplet size distribution with increasing stirring times, from 5 to 60 min, at an agitation speed of 700 rpm.
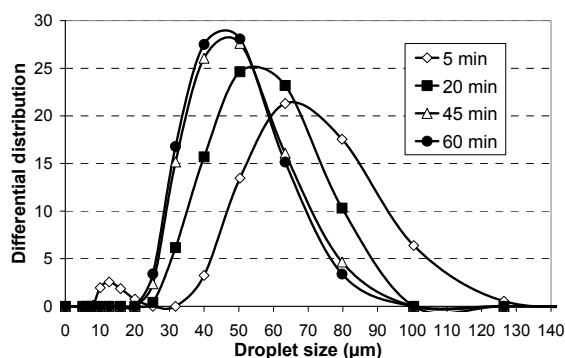

Fig. 1 – Evolution of the droplet size distribution with stirring time (agitation speed N=700 rpm; ClBu weight fraction Φ=2 wt%; [KP08]=0.1 wt%/ClBu).

It can be noticed in Figure 1 that from an initial broad size distribution and an average droplet size of 70 μm, these emulsion characteristics decrease progressively with the agitation time. In fact, both size distribution and average size level off with stirring time and reach almost constant values after 50–60 minutes of stirring, which correspond to the dynamic equilibrium between the breakage rate of

the droplets and their coalescence rate. The evolution towards the steady state can furthermore be explained by the time required for the PVA molecules to be adsorbed onto the droplet surface, to rearrange themselves into an equilibrium conformation at the ClBu/water interface and thus to protect the droplets from coalescence.[2]

The decrease of the average droplet size D_{50} versus agitation time, and at different agitation speeds (500-800 rpm) is shown in Figure 2.
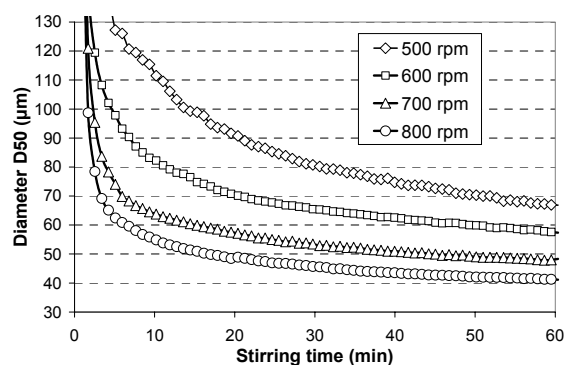

Fig. 2 – Mean droplet diameter D_{50} as a function of stirring time for different agitation speeds (Φ=2 wt%; [KP08]=0.1 wt%/ClBu).

As expected, the droplet size decreases more rapidly, and smaller droplets are obtained, by increasing the agitation speed.

Influence of the PVA concentration on the ClBu droplet size distribution and ClBu/water interfacial tension.

The influence on the ClBu droplet size of the PVA concentration was studied in the range of 0.025 to 1 wt% with respect to ClBu, which corresponds to the usual stabilizer concentration used in emulsion and suspension polymerization. The evolutions of the mean droplet diameter D_{50} and of the distribution width $(D_{90}–D_{10})$ in function of the PVA concentration are displayed in Figure 3.
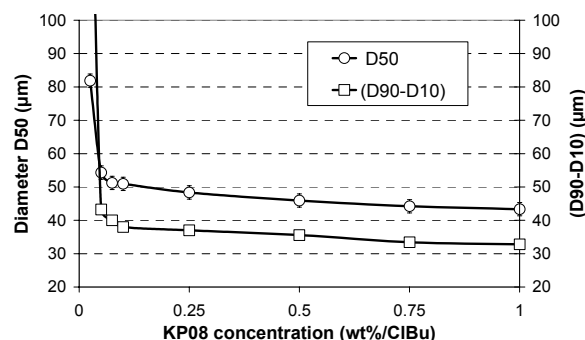

Fig. 3 – Evolution of the mean droplet diameter D_{50} and distribution width $(D_{90}-D_{10})$ in function of the KP08 concentration (stirring time=60 min; N=700 rpm; Φ=2 wt%).

From Figure 3, it appears that the average droplet size decreases sharply at low PVA concentrations. For the PVA concentrations from 0.5 to 1%, the D_{50} value levels off at around 43 μm. A similar trend can be observed for the distribution width.

At this point, it was of interest to check if there is any correlation between the emulsion droplet size and the ClBu/water interfacial tension in the presence of PVA. The interfacial tension, determined by the pendent drop technique, as a function of time and PVA concentration is shown in Figure 4.
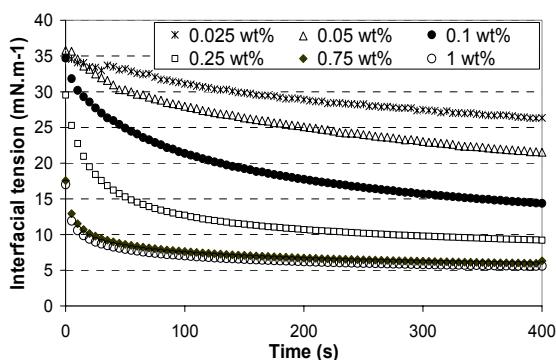

Fig. 4 – Evolution of the interfacial tension ClBu/water as a function of time for different concentrations of KP08.

With increasing PVA concentrations, the interfacial tension decreases from 27 mN.m^{-1} to 6 mN.m^{-1} for 1% of PVA. The time needed for the system to reach equilibrium also decreases at higher PVA concentrations. This behaviour is typical of surfactive polymeric compounds, which have a lower mobility and therefore need a certain time to get adsorbed in an equilibrium conformation on the liquid/liquid interface.[14]

The mean droplet size D_{50} and the distribution width (D_{90}–D_{10}) have been plotted as a function of the equilibrium values of the interfacial tension (cf. Figure 5).
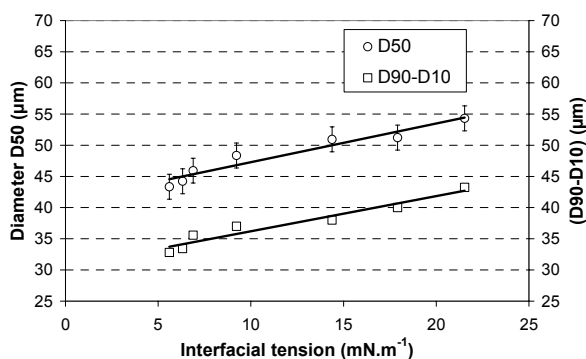

Fig. 5 – Correlation between the mean diameter D_{50}, the distribution width (D_{90}-D_{10}) and the interfacial tension.

From Figure 5, it can be concluded that there is definitely a direct linear correlation between the mean droplet size D_{50}, the distribution width (D_{90}-D_{10}) and the interfacial tension.

Influence of the type of PVA on the ClBu droplet size distribution.

KH17, having a hydrolysis degree ($\overline{DH}$) and a molar mass higher than those of KP08 (cf. Table 1), has also been tested as stabiliser of the ClBu/water emulsions. Figure 6 presents the evolution of the mean droplet diameter D_{50} in function of the concentration of KP08 and KH17. The size distributions of these two systems are given in Figure 7 at PVA concentrations of 0.05 and 1 wt%/ClBu respectively.
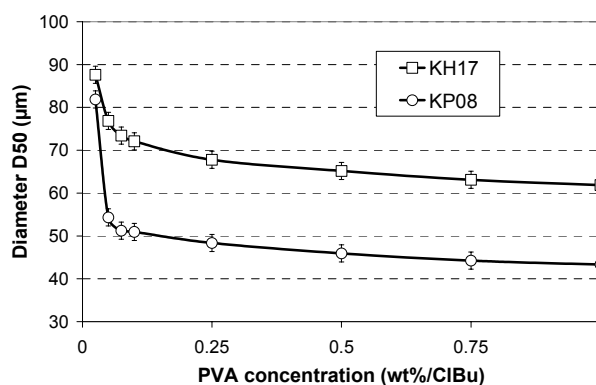

Fig. 6 – Evolution of the mean diameter D_{50} in function of the concentration of KP08 and KH17 (stirring time=60 min; N=700 rpm; Φ=2 wt%).
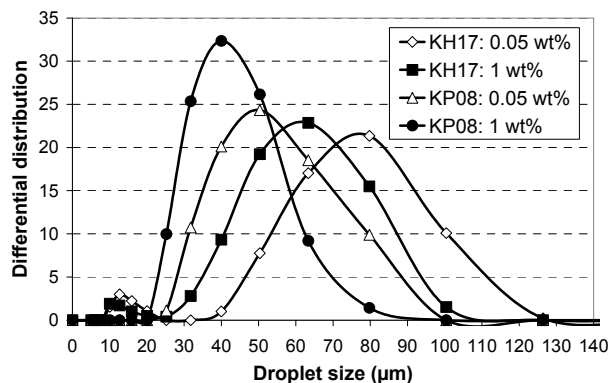

Fig. 7 – Droplet size distribution of emulsions stabilised with 0.05 and 1 wt%/ClBu of KP08 and KH17 (stirring time=60 min; N=700 rpm; Φ=2 wt%).

KP08, with a lower $\overline{DH}$ (72 mol%) than KH17 (78 mol%), allows to decrease more the mean droplet size and size distribution than KH17. Owing to its more appropriate hydrophilic/

hydrophobic ratio, KP08 is preferably adsorbed at the ClBu/water interface and therefore decreases the interfacial tension and the droplet sizes.

EXPERIMENTAL

Material

1-chlorobutane (ClBu), supplied by Acros, was chosen as model fluid of vinyl chloride monomer, because it has characteristics similar to VCM (densities, solubility parameters...), with the advantages of easier handling and less toxicity.[15,16] The continuous phase of emulsions consisted of demineralised water with partially hydrolysed poly (vinyl acetate) (PVA). The two PVA used were commercial samples of Gohsenol KP08 and Gohsenol KH17 supplied by Nippon Gohsei. Their principal characteristics, determined using ^{1}H and ^{13}C NMR and SEC are presented in the Table 1.

Table 1

Principal characteristics of KP08 and KH17

	KP08	KH17
$\overline{DH}$ (mol%)	72±1	80±1
$\overline{M_W}$ (g.mol^{-1})	39200	117250
$\overline{M_n}$ (g.mol^{-1})	19600	54280
$\overline{n}_{(VOH)}$	7.7±0,2	8.5±0,2
$\overline{n}_{(VAc)}$	3.9±0,1	3.5±0,1

The hydrolysis degree $\overline{DH}$ and the average sequence lengths of vinyl alcohol $\overline{n}_{(VOH)}$ and vinyl acetate $\overline{n}_{(VAc)}$ were determined using ^{1}H NMR in dimethylsulphoxide (DMSO)-d$_6$ at 70°C according to Van der Verden and Beulen.[19] The SEC measurements were performed in tetrahydrofuran (THF) at 30°C using reacetylated samples as recommended by Bugada and Rudin[19] and the "universal calibration technique"[4] with polystyrene standards was applied for the calculation of $\overline{M_n}$ and $\overline{M_W}$.

Procedure

ClBu/water emulsions were prepared in a 1 litre round-bottomed glass reactor fitted with two equally spaced stainless steel baffles. The agitator was a stainless steel three-curved-blade turbine. The temperature of emulsions was kept at 20°C inside the tank by mean of a water circulation through the vessel jacket.

In a typical experiment, the reactor is first filled with demineralised water and the required amount of PVA, previously dissolved by heating at 70°C in water at a concentration of 0.1 or 1 wt%. The ClBu, with a weight fraction Φ of 0.02 (2 wt%) is added to the vessel and the agitation speed is adjusted to 700 rpm, except when the effects of stirring speed were studied. The circulation of the emulsion is performed from the bottom of the reactor to the measuring cell of the granulometer by means of a low shear peristaltic pump and then brought back in the reactor. It has been calculated that the circulation of the emulsion through the circulation loop lasts about 30 seconds that corresponds to a residence time inside the measuring cell of about 1 second.

The measurement of the droplet size distribution is carried out by an on-line acoustic granulometer OPUS, commercialised by Sympatec. The principle of the acoustic spectroscopy is based on the measurement of the attenuations of ultrasonic waves (1-120 MHz) by the emulsion droplets. The software, designed by Sympatec transforms the measured attenuations into the corresponding size distribution of the droplets and to the evolution of mean diameters in function of time. Details about the principles of acoustic spectroscopy and the characteristics of the OPUS system can be found elsewhere.[9-11] The interfacial tensions ClBu/water in the presence of PVA are determined by a pendent drop technique (Krüss DSA 100), based on the form of the droplet at equilibrium.[20]

CONCLUSION

Acoustic spectroscopy appears to be a valuable technique for the on-line particle size determination of oil/water emulsions. However for ClBu/water emulsions in the particle size range of 20-100 μm, and therefore also for the corresponding VCM/water emulsions, this technique is only applicable for relatively low ClBu/water ratio, typically up to 2-3% of ClBu. In this limited concentration range, it could be shown that polymeric stabilisers, such as PVA, migrate relatively slowly to the ClBu/water interface. The correlation between the droplet characteristics, average droplet size and size distribution, and the interfacial tension of the two-phase system could clearly be established. Further studies are in progress to test the efficiency of various PVAs and PVA combinations.

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