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Chemical Engineering Research and Design

journal homepage: [www.elsevier.com/locate/cherd](http://www.elsevier.com/locate/cherd)

# Influence of poly(vinyl alcohol) molecular weight on drop coalescence and breakage rate



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## ARTICLE INFO

### Article history:

Received 20 July 2015

Accepted 15 October 2015

Available online 25 October 2015

### Keywords:

Polyvinyl alcohol

Drop size distribution

Interfacial tension

Population balance equation

Multifractal breakage model

Multifractal coalescence model

## ABSTRACT

The influence of poly(vinyl alcohol), PVA, molecular weight on drop breakage and coalescence in stirred liquid–liquid dispersion was considered. Three types of PVA of the same degree of hydrolysis 88% and different molecular weights in the range 13,000–186,000 were used in experiments. Molecular weight affects steric forces, interfacial tension and surface viscosity, which all have an influence on drop size distribution. PVA of lower molecular weight reduces the interfacial tension more effectively while the adsorption of high molecular weight PVA is slower and more complicated. Drop interfaces can remain partially mobile for polymer concentration as small as 0.001 wt% or they can be significantly immobilized for PVA concentration  $c \geq 0.002$  wt%. Drop size distributions were predicted using multifractal breakage and coalescence models. Loss of stabilizing properties of PVA of highest molecular weight at high impeller speed was observed which can be explained by unfavorable molecule conformation in such conditions.

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## 1. Introduction

Liquid–liquid dispersions are commonly used in industrial processes such as heterogeneous chemical reactions, extraction and suspension polymerization. Such systems are extremely complex due to changes of surface properties which can be caused by surfactant adsorption, liquid viscosity or small solid particles. Therefore, precise investigation of dispersion behavior is still one of the main scientific tasks. Surfactants, i.e. surface active agents reduce the interfacial tension and lead to production of smaller drops due to increased breakage rate and decreased coalescence rate. Hence, higher total interfacial area and homogeneity of dispersion are possible to be obtained. Due to the stabilizing properties surfactants of low molecular weight (for example Tween series, Brij series, SDS) as well as surface active polymers (poly(vinyl alcohol), poly(vinyl pyrrolidone), Pluronic, etc.) can be used as emulsifiers in liquid–liquid systems. Simple or multiple emulsions in food and pharmaceutical industry are mainly stabilized by biopolymers such as gelatin, egg yolk, starch and proteins (Dalglish, 1997;

Dłuska and Markowska-Radomska, 2010; Li et al., 2013; Qiu et al., 2015; Schuch et al., 2015).

Surface active polymers are a group of surface active agents which are used as alternative to the low molecular weight non-ionic and ionic surfactants. Their main advantage results from their strong adsorption and steric stabilization. Moreover, polymers can be applied in the presence of high electrolyte concentrations and at high temperatures (Tadros et al., 2004). The possible stabilization mechanisms include steric hindrance, Gibbs–Marangoni effect and increased surface viscosity. Higher surface viscosity leads to drop surface immobilization and reduced coalescence rate. Therefore, the viscosity effect can be one of the major reasons of increased stability of liquid–liquid dispersion (Lochhead and Rulison, 1994; Rulison and Lochhead, 1995; Dreher et al., 1999), especially when polymer concentration is high (Morgan, 2001; He et al., 2004). In the case of two other mentioned mechanisms, it is postulated that the main stabilizing effect results from the steric hindrance between drops, not from the Gibbs–Marangoni effect which is rather offered by

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<http://dx.doi.org/10.1016/j.cherd.2015.10.027>

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### Nomenclature

$A$	Hamaker constant (J)
$a$	film radius (m)
$a_v$	total interfacial area per total volume ( $\text{m}^2 \text{m}^{-3}$ )
$b$	exponent on the Weber number
$C$	constant in the coalescence model
$C_g, C_x$	constants in the breakage model
$c$	polymer concentration (wt%)
$D$	impeller diameter (m)
$D_t$	tank diameter (m)
$d$	drop diameter (m)
$d_{32}$	Sauter diameter (m)
$d_{jk}$	$=(d_j + d_k)/2$
$E(v, v')$	energy, increase in energy (J)
$f(\alpha)$	multifractal spectrum
$g(d)$	breakage rate ( $\text{s}^{-1}$ )
$H$	tank height (m)
$h_c$	critical film thickness (m)
$h_0$	initial film thickness (m)
$h(d, d')$	drop collision function ( $\text{m}^3 \text{s}^{-1}$ )
$L$	integral scale of turbulence (m)
$N$	impeller rotational speed ( $\text{s}^{-1}$ )
$n(v, t)$	number density function of drops ( $\text{m}^{-6}$ )
$R$	drop radius (m)
$R_{eq}$	equivalent radius (m)
$T$	temperature ( $^{\circ}\text{C}$ )
$t_{eff}$	effective adsorption time (s)
$t_d$	time of drop formation (s)

### Greek symbols

$\alpha$	multifractal exponent
$\alpha_{min}$	minimum value of the multifractal exponent $\alpha$
$\alpha_x$	upper bound of the multifractal exponent $\alpha$
$\beta(v, v')$	daughter drop distribution function ( $\text{m}^{-3}$ )
$\gamma$	coefficient of virtual mass
$\varepsilon$	turbulent energy dissipation rate ( $\text{m}^2 \text{s}^{-3}$ )
$\lambda(d, d')$	coalescence efficiency
$\mu$	dynamic viscosity (Pa s)
$\nu(v')$	number of daughter drops
$\rho$	density ( $\text{kg m}^{-3}$ )
$\sigma$	static interfacial tension ( $\text{N m}^{-1}$ )
$\nu$	drop volume ( $\text{m}^3$ )
$\phi$	dispersed phase volume fraction

### Subscripts

$C$	continuous
$D$	dispersed
$L$	larger
$S$	smaller
$imp$	impeller zone
$bulk$	bulk zone

low-molecular weight nonionic surfactants (He et al., 2002, 2004). The steric interaction is generated when the film thickness between two approaching drops becomes smaller than  $2L_b$ , where  $L_b$  is the thickness of the polymer brush layer. The disjoining pressure (which results from the steric effect),  $\Pi$ , in a good solvent can be calculated from the Alexander-de Gennes equation (Alexander, 1977; de Gennes, 1987). However, it should be kept in mind that proposed model is only an approximation, due to the assumption that each adsorbed molecule is anchored at only one end to the surface. The real adsorption

of polymers may significantly differ from that simplified and particular case.

Another feature differing polymers from low-molecular weight surfactants results from their ability to conform after anchoring at the interface. The adsorption process is, therefore, a three-step process, i.e., apart from diffusion and adsorption steps (just like for low-molecular weight surfactants) the additional third step, i.e. a molecule conformation, is distinguished. Polymer unfolds and conforms after adsorption in order to reach a maximum possible surface coverage. As a result, a polymer chain may form the sequences of loops, trains and tails. The efficiency of this process is dependent on polymer molecular weight, degree of hydrolysis and bulk polymer concentration (Morgan, 2001; Tadros et al., 2004; He et al., 2004). The higher the polymer molecular weight is, the more retarded the adsorption process becomes (Lankveld and Lyklema, 1972; Morgan, 2001). According to Prasetya (2001), polymers of higher molecular weight are more complicated in their adsorption at the interface. In addition, their adsorption is very slow because long chains sterically hinder anchoring of other molecules.

Droplets suspended in a continuous phase are affected by disruptive and stabilizing stresses. The type of stresses acting on drops is dependent on drop diameter  $d$  (which classifies the drop size as falling to the inertial or viscous subrange of turbulence) and dispersed phase viscosity. For liquid-liquid dispersions of low dispersed phase viscosity and for drops bigger than the Kolmogorov microscale (which are in general present in a stirred tanks) only turbulent stresses generated by the dynamic pressure fluctuations and stabilizing shape-restoring stresses proportional to the interfacial tension should be taken into account. Additional disruptive stress due to interfacial tension difference (Koshy et al., 1988) identified in dispersion containing very small molecular weight surfactants (Bak and Podgórska, 2012; Podgórska and Marchisio, 2015) is not expected in the case of high molecular weight polymers used in this work.

Drop breakage occurs when the local instantaneous stresses generated by the turbulent motion in a continuous phase exceed shape-restoring stresses. This process is privileged in the initial stage of dispersion mixing or after increasing the impeller speed. Moreover, drop breakage takes place mainly in the impeller zone because the most of supplied energy is there dissipated and turbulent eddies are vigorous enough to break the drop. One can expect that even if the drop size is significantly reduced by surfactant, drops present in the impeller zone will be still larger than the Kolmogorov microscale. Mathematical models for drop breakage based on the classical Kolmogorov theory have been considered and developed by many researchers. One of the first models was derived by Ross and Curl (1973). A phenomenological model was proposed by Coualoglou and Tavlarides (1977) for dispersions containing drops of low viscosity from inertial subrange of turbulence. Further model's improvements were introduced for example by Tsouris and Tavlarides (1994). Nevertheless, the Coualoglou and Tavlarides model (1977) was, and still is widely used by many researchers for interpretation of experimental data. The tank scale and its influence on the breakage rate were taken into account for the first time by Konno et al. (1983). The breakage region in a stirred tank where break-up is possible was assumed to consist of regions of the isotropic and non-isotropic turbulence. Narsimhan et al. (1979) proposed a stochastic breakage model in which a drop is interpreted as the one-dimensional harmonic oscillator. Another concept was used by Martinez-Bazan et al. (1999), who postulated that the acceleration of interfaces during drop deformation is proportional to the difference between disruptive forces and restoring ones. In many cases models based on the Kolmogorov theory give good agreement between predicted and experimental data. However, some experimental data also exist for which these models are not sufficient (Konno et al., 1983; Konno and Saito, 1987; Baldyga and Bourne, 1995; Kuriyama et al., 1996; Lam et al., 1996; Baldyga et al., 2001, among others). The phenomena such as: drift of transient drop size distributions at long agitation times, a drift of the exponent  $b$  on the Weber number ( $d_{max} \propto We^b$ ) from  $-0.6$  to  $-0.93$ , scale-up effect which reveals in a faster drop breakage in a larger tank when geometric similarity and constant mean energy dissipation rate are maintained can be explained by taking into account

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