ABSTRACT

The condition of oligo-micelle formation of sodium di-isodecyl sulfosuccinate (SDIDS) emulsifier in hydro-alcoholic solutions is used to study particle formation of vinyl chloride emulsion polymerization in a batch reactor. The change on micellization behavior was investigated by critical micelle concentration (CMC) and zeta potential parameters. To detect the occurrence of secondary nucleation or particle aggregation, or both, the particle size and number of particles were investigated as a criterion for the particle nucleation and growth process. The results showed the alcohol content as a co-solvent has a strong effect on the oligo-micelles formation and emulsion polymerization performance. Namely, decreasing the alcohol content and increasing the anion content in the SDIDS samples increased the overall reaction rate and latex stability. This also decreased the chain growth rate, the particle size, and the coarse particle formation. Also, the results showed that different condition of oligo-micelle formation would lead to different particle growth history.

Keywords: Emulsion polymerization; poly (vinyl chloride); double-chain emulsifier; oligo-micelle; particle growth.

INTRODUCTION

The choice of the proper emulsifier to prepare stable polyvinyl chloride (PVC) latex by emulsion polymerization (E-PVC) is a complex problem because the emulsifier greatly affects the reaction kinetics and the physico-chemical and colloidal properties of the final latex [1]. Several works have been reported in the literature on emulsifier type on E-PVC polymerization [2-8] and it is one of the key important operating variables in this specific polymerization [1].

Both mono- and dialkyl sulfosuccinates are one of the main anionic emulsifiers used in E-PVC [9-12]. They have excellent wetting, emulsifying, dispersing, and foaming properties. [11-12]. Typically, di- alkyl sulfosuccinate emulsifier groups are used as viscosity depressant in emulsion PVC [10]. Also from literature it is understood that emulsifiers from sulfosuccinate group give medium size particles [9]. Sodium di-isodecyl sulfosuccinate (SDIDS) is an anionic double-chain sulfonate emulsifier with
long side-chain length (around 10 carbons) in hydro-alcoholic solutions that are widely used in the E-PVC [10-12].

The double-chain emulsifier with long side-chains by a critical side-chain length (around six carbons) like SDIDS has the potential to form highly ionized small aggregates, regarded as oligo-micelles [13]. For this double-chain micelle, it has been reported that conductivity increases when micelles start to form which is in contrast for the single chain [14, 15] and double-chain with short-chain [13] emulsifiers.

On the other hand, the presence of short-chain alcohols as co-solvent in the emulsion system has shown an impact on the solubility, liquid structure and hydrophobic interactions between emulsifier and water molecules that are involved in the micellization process. [16-22]. The effects involved in the changes of micellization parameters such as critical micelle concentration (CMC), the micelle size and etc. are depended on the partition of alcohols between micelles and intermicellar solution [16, 17, 19, 20]. For example, while methanol has shown an increase in the CMC, propanol has played a minimum dependency on overall alcohol content on it [16, 17].

Isopropyl alcohol is a commonly used solvent in the synthesis of SDIDS [11, 12]. It is a common process in industry that the chemical source providers change the concentration of this alcohol occasionally in their products for different reasons. In the case of SDIDS emulsifiers with more than one supplier, different compositions of alcohol and aqueous phases has been observed in which have shown variation of the latex quality in E-PVC processes.

Carefully considering the relevant literature [13, 16, 17, 19, 20], reveals that the presence of isopropyl alcohol as short-chain alcohol could have a key role on micellization process of SDIDS as a double-chain emulsifier with a long side chain.

In spite of various articles published on E-PVC, i.e. the significant amount of research works which have been devoted for well-characterized single chain emulsifiers such as SDS and SDBS [2, 3,5,7, 23-28] and also limited reports on double chain emulsifiers [3, 9], to the best of our knowledge, no report is available in the open literature attributed to the presence effect of short-chain alcohols on micellization process of anionic double-chain sulfonate emulsifiers in hydro-alcoholic solutions in terms of VCM emulsion polymerization.

The principle objective of the work presented in this paper is to illustrate the source of quality variation of an industrial E-PVC process which associated to SDIDS emulsifiers in hydro-alcoholic solution with more than one supplier and dissimilar compositions, while industrial materials and recipe on a pilot-scale reactor were employed. This work addresses the issue of alcohol content in a hydro-alcoholic solution of SDIDS samples which impact on the latex properties of E-PVC. The changes observed in the CMC and zeta potential parameters have been used to interpret the interactions between alcohol and SDIDS.
EXPERIMENTAL

Materials

VCM was supplied by Arvand Petrochemical Company, with a purity of above 99.98% measured by gas chromatography. Three SDIDS samples \((C_{24}H_{45}NaO_7S)\) in hydro-alcoholic solution with dissimilar compositions (Table 1) and sodium pentadecan-sulfonate (SPS) (Lanxess), were employed as emulsifiers in the current study. Also, potassium persulfate (KPS) (Proxy chem) and disodium phosphate (DSP) (Zohal shimi) were used as the initiator and buffer, respectively. All the chemicals were used as supplied without further purification. Demineralized (DM) water (with conductivity below 2 μS/cm) was used throughout the work for the batch polymerizations. Cyclohexanone (Merck) was utilized as the solvent for K-value measurements.

Polymerization procedure

Polymerizations reaction were performed in a 15 L jacketed stainless steel reactor, equipped with flat turbine (four-blade) impeller, two baffles, and a magnetic seal derives (MSD) to prevent gas leakage. All the reaction temperature was constant and kept down at 50.0 \((±0.3)\) °C. The stirring speed was constant and set at 150 rpm. In all reactions, the weight ratio of KPS and DSP to the VCM were 0.003 and 0.0012, respectively. Also SPS and SDIDS concentrations were 1.81 and 14.74 g L\(^{-1}\), respectively, based on the total volume of the water phase.

Zero-time of the reaction was considered when the reactor temperature was 49.0°C. For all reaction runs, the ratio of water/monomer was 1.25 (by weight). With a sample connection which was provided at the bottom of the reactor, latex samples were taken for monitoring the polymerization reaction at various times. The pH of the latex was monitored during the reaction by litmus paper. To have the same conversion yield, the pressure drop to 5 barg was kept constant in all runs as the criterion for ending of the reaction, unless the reaction temperature control was not possible. At the end of the reaction, coarse matter content (particles bigger than 300 µm in size) as a qualitative character of the final latex is used as the main parameter which indicates the reaction stability and is described by % wt coarse matter in the final latex.

Table 1. Composition of the three SDIDS samples: (a) SDIDS1, (b) SDIDS2, (c) SDIDS3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SDIDS1</th>
<th>SDIDS2</th>
<th>SDIDS3</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anion content</td>
<td>65.8</td>
<td>68.5</td>
<td>72.4</td>
<td>Emulsifier</td>
</tr>
<tr>
<td>Water (%wt)</td>
<td>19.5</td>
<td>24.1</td>
<td>20.2</td>
<td>Aqueous phase</td>
</tr>
<tr>
<td>Isopropyl alcohol (%wt)</td>
<td>12.5</td>
<td>4.5</td>
<td>3.9</td>
<td>Alcohol phase</td>
</tr>
<tr>
<td>Isodecyl alcohol (%wt)</td>
<td>2.2</td>
<td>2.9</td>
<td>3.5</td>
<td>Co-emulsifier (SDIDS basis alcohol)</td>
</tr>
</tbody>
</table>

Latex Characterization
Solid content (SC) of the latexes were measured gravimetrically during the reaction for conversion calculation [29, 30]. K-values were determined according to ISO 1628 with cyclohexanone as solvent [26, 31]. Particle size and its distribution (PSD) were measured by scanning electron microscopy (SEM) (TEScan, VEGA 3) technique and proceeded with image analysis software (Image 1.51j8). At least 430 particles were measured on the micrographs for statistical validation of the results [32]. Also, the PSD curves were plotted based on frequency versus particle size. The necessary parameters were derived from referred literature and the calculations were based on the mentioned formulas as shown in Table 2.

The $X_c$ (critical conversion) was considered as 0.7 for all runs. The $\rho_m$ (density of monomer) = 850 g L$^{-1}$, $\rho_p$ (density of polymer) = 1380 g L$^{-1}$, and $M_M$ (molecular weight of monomer) = 62.5 g mol$^{-1}$ [3, 33, 34]. $C_{MP}$ was calculated approximately equal to 5.6 mol L$^{-1}$ (in the current study). Also, coefficient of propagation rate ($K_p$) is about 11000 mol$^{-1}$ s$^{-1}$ at 50 °C for VCM polymerization [28, 34]. $N_p$ was calculated by substitution of the calculated $d_{pswol}$ instead of $d_v$.

**RESULTS AND DISCUSSION**

**Characterization of the Emulsifier**

The composition of the three selected SDIDS samples, and hereinafter named SDIDS1, SDIDS2 and SDIDS3, which extracted from thermogravimetric analysis (TGA), METTLER, 20°C.min$^{-1}$ under nitrogen atmosphere, are listed in Table 1. Due to the different content of SDIDS samples such as alcohol, water, and anion content, it has the potential to change micellar properties [16-21] which are very important in emulsion polymerization [25, 35].

The results in Table 1 show increasing trends for isodecyl alcohol (%wt) and anion content (%wt), while it shows a decreasing trend for isopropyl alcohol (%wt) by going from SDIDS1 to SDIDS3. Isopropyl alcohol is a short chain alcohol and could act as a co-solvent which is preferentially solubilized in the palisade layer and decreases the dielectric constant of water upon solubilization of alcohol [16, 17, 19-21] while the remaining isodecyl alcohol which is a longer chain alcohol could act as a co-emulsifier in micellization process [8, 21, 37-39] by solubilization in both the palisade layer and the micelle hydrophobic core [16, 17, 21], and consequently changing the emulsion parameters.
Table 2. The necessary formula derived from referred literature for kinetic studies.

<table>
<thead>
<tr>
<th>No.</th>
<th>Description</th>
<th>Formula</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Overall mass conversion</td>
<td>( X_m(t) = \frac{SC(t) - SC(initial)}{SC(final) - SC(initial)} )</td>
<td>[29, 30]</td>
</tr>
<tr>
<td>2</td>
<td>Overall polymerization rate</td>
<td>( R_p(t) = \frac{d\theta(t)}{dt} = \frac{\rho_p dX_m(t)}{d t} )</td>
<td>[29, 30]</td>
</tr>
<tr>
<td>3</td>
<td>Volume average diameters</td>
<td>( d_v = \left( \frac{\sum n_i d_i^3}{\sum n_i} \right)^{1/3} )</td>
<td>[23, 36]</td>
</tr>
<tr>
<td>4</td>
<td>Total number of particles per unit volume of the aqueous phase</td>
<td>( N_p = \frac{6}{\pi} \frac{\rho_p}{\rho_v} \frac{P}{W} \times \frac{1}{d_v^3} )</td>
<td>[23, 30, 36]</td>
</tr>
<tr>
<td>5</td>
<td>Weight ratio of polymer to water</td>
<td>( \rho = \frac{M}{W} \times X_{0v} )</td>
<td>[23, 30, 36]</td>
</tr>
<tr>
<td>6</td>
<td>Total number of polymer particles per unit mass of the latex</td>
<td>( \bar{n} = \frac{N_p \rho_{av}}{\rho_v \rho_p C_M} )</td>
<td>[5]</td>
</tr>
<tr>
<td>7</td>
<td>Average number of growing chain per particle</td>
<td>( C_{MP} = \frac{(1 - X_c) \rho_M}{(1 - X_c + X_c \frac{\rho_P}{\rho_v}) M_M} )</td>
<td>[28, 34]</td>
</tr>
<tr>
<td>8</td>
<td>Overall monomer concentration in the polymer particles at interval II</td>
<td>( C_{MP} = \frac{(1 - X_c - X_c \frac{\rho_D}{\rho_P}) M_M}{100 - X_c} \times C_{MP} )</td>
<td>[29]</td>
</tr>
<tr>
<td>9</td>
<td>Overall monomer concentration in the polymer particles at interval III</td>
<td>( d_{p,swell} = d_v \left( 1 - \frac{M_M C_{MP}}{\rho_M} \right)^{-1} )</td>
<td>[29]</td>
</tr>
</tbody>
</table>

**CMC Determination by Conductometry**

A 5 ring conductivity measuring with a cell constant 0.7 cm\(^{-1}\) of Metrohm (Switzerland) conductivity meter was used to monitor the conductivity during titrations. The conductivity was measured stepwise by introducing an aliquot volume of the mother solution into ultra-pure water. Ultra-pure water with the conductivity of less than 0.5 µ S/cm was used for preparing all solutions. The temperature was controlled at 25°C ± 0.5 °C.

For CMC determination of double- chain emulsifiers with long side-chains (more than around six carbons), differential conductivity which is defined as \( d\kappa /dC_E = (\kappa_2 - \kappa_1) / (C_{E2} - C_{E1}) \) vs. \( C_E^{0.5} \) plot [13] is used in place of the traditional conductivities i.e., the \( \kappa \) vs. \( C \) plot [14, 15]. The transitional region between the first minimum and maximum of the plot is named CMC region and are defined by \( C_{MC_L} \) and \( C_{MC_H} \), respectively [13]. This behavior is observed for SDIDS samples (Fig. 1a) and the obtained results are summarized in Table 3.

**CMC Determination by Tensiometry**

Tensiometry measurement was made at 25°C using a Krüss K12 tensiometer under atmospheric pressure by the ring method. The platinum ring was thoroughly cleaned and then flame-dried before each measurement. When a series of at least 3 measurements were completed, the processor
calculated the average value of the surface tension in mN m$^{-1}$ (Fig. 1b). The obtained CMC results are presented in Table 3.

CMC reported from tensiometry is among the CMC$_{L}$ and CMC$_{H}$, hence it could be concluded that the CMC reported by the two methods are reliable. CMC$_{L}$ data in Table 3 (among the same data between SDIDS1 - SDIDS3) represents the same trend as isodecyl alcohol (% wt) and anion content in Table 1.

![Figure 1a](image1.png) ![Figure 1b](image2.png)

**Figure 1.** Characterization results of the three SDIDS samples: (a) concentration dependence of $d\kappa /dC_E$, (b) surface tension measurements, (c) electrophoretic mobility distribution, (d) zeta potential distribution.

In addition, electrophoretic mobility and zeta potential of the samples were determined by Zetasizer Ver. 6.01, Malvern Instruments Ltd at room temperature (Fig. 1 c&d and Table 3). The concentration of emulsifiers in water was about 14.74 g L$^{-1}$ same as polymerization recipe. The distinguished bimodal distribution in both electrophoretic mobility and zeta potential parameter for SDIDS1 (Fig. 1c&d) obviously indicates that two sizes of emulsifier aggregates exist in the media. It is assumed that the first peak is related to the smaller size structure like oligo-micelle which has been formed more for SDIDS1, while the second peak indicates near to micelle structure, similar to SDIDS2 & SDIDS3.
Fig. 1a shows CMC_L for SDIDS1 is noticeably lower than for SDIDS2 and SDIDS3. It also shows that CMC range (CMC_L & CMC_H) for SDIDS1 is wider than their amounts for SDIDS2 & SDIDS3. It is guessed that higher isopropyl alcohol content, especially for SDIDS1, lowers the dielectric constant of the medium and it causes the tendency for the formation of smaller aggregates [17, 19, 20]. On the other hand, the charged head groups are further apart due to smaller aggregates, hence the observation of lower zeta potential obtained for SDIDS1, is assumed to be the reason for a more closely packed structure for this sample. Furthermore, by decreasing the size of the micelles at higher alcohol contents, the self-diffusion coefficient can increase [20] and it is the main source of the change in the mobility for SDIDS1. For SDIDS2 & SDIDS3 with lower alcohol content, lower self-diffusion is expected. However, SDIDS3 with higher anion content and lower water content have upper mobility at the same mass concentration in comparison with SDIDS2.

### Table 3. CMC, electrophoretic mobility and zeta potential parameters of the three SDIDS samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SDIDS1</th>
<th>SDIDS2</th>
<th>SDIDS3</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMC (a) by Conductometry [mg L⁻¹]</td>
<td>6.17 &amp; 10.32</td>
<td>8.45 &amp; 11.85</td>
<td>8.77 &amp; 10.81</td>
</tr>
<tr>
<td>CMC by Tensiometry [mg L⁻¹]</td>
<td>9.41</td>
<td>9.37</td>
<td>10.58</td>
</tr>
<tr>
<td>Electrophoretic Mobility [μmcm/Vs] (b)</td>
<td>-7.30</td>
<td>-5.11</td>
<td>-5.37</td>
</tr>
<tr>
<td>Zeta Potential [mV] (b)</td>
<td>-92.7</td>
<td>-65.2</td>
<td>-68.5</td>
</tr>
</tbody>
</table>

(a) Differential conductivity method (CMC_L and CMC_H) 
(b) Determined by Zetasizer

### Influence on the polymerization

A unique recipe was applied to study the behavior of the three SDIDS samples on the batch emulsion polymerization of VCM.

**Conversion and Kinetic**

Fig. 2a shows the time evolution versus conversion. The overall slope of the linear portion of the conversion-time at the interval II was used as dx/dt for calculation of $R_p$ (Table 4). Almost a constant rate of reaction was observed from 10 – 70 % of monomer conversion for SDIDS2 and SDIDS3 (Fig. 2a) however, SDIDS1 has shown different behavior in conversion-time from the first to the end of the reaction almost in a stop and jumping (step-like) behavior.

It seems that SDIDS1 with higher alcohol content has the potential for production of oligo-micelles with very small aggregates in each period of time which do not qualify them as micelles for particle nucleation but act more as available emulsifier supplier with higher mobility. Actually, when an alcohol exists in an emulsifier micellar solution, it disrupts the three dimensional network structures of the water; and water molecule replace with isopropyl alcohol molecule [18, 20], so the amphiphilicity of the emulsifier decreases and it does not have the ability to form micelles in the
alcohol dominant media, and as a result the fraction of monomeric emulsifier increases in the media [18], ultimately, equilibrium is reached between the micellar and alcohol phase [18, 20]. Actually, with increasing alcohol concentration, the electrostatic repulsions between head group of emulsifier in micellar core is shown to be decreased [19]. Also, it is reported that micelles could even disappear when enough alcohol is added to the emulsifier solution [17]. By consumption of emulsifier molecules for stabilizing the growing particles, although emulsifier concentration in reaction media decreases, the alcohol concentration remains constant. Hence, the ratio of alcohol to emulsifier gradually reaches to a new condition for re-construction of oligo-micelle with small aggregate. Therefore, in each equilibrium states, the new balance between required free emulsifier for both polymer particle stability and series of oligo-micelles, which are saturated by alcohols, are formed due to new thermodynamic condition. The step-like behavior in the conversion curve for SDIDS1 (Fig. 2a) could be attributed to the successive equilibrium time reached for emulsifier molecules partitioning between the oligo-micelle, polymer particles and free emulsifier in the media.

![Figure 2](image_url)

**Figure 2.** Batch results of the three SDIDS samples: SDIDS1, SDIDS2, SDIDS3: (a) conversion vs. time, (b) PSD curves of the latex at 270 minutes, (c) PSD curves of SDIDS3 at 180, 270 and 360 minutes, (d) PSD curves of SDIDS1 at 180, SDIDS2 at 270, and SDIDS3 at 360 minutes.
Table 4 shows that $R_p$ values differ for the three samples and with supposing a trend, it is increasing from SDIDS1 to SDIDS3. Similar trends are observed for anion content, while the opposite trend is reported for isopropyl alcohol content (Table 1). The overall conversions are nearly the same for all three samples at time 180 minutes of the reactions however at time 270 minutes, the SDIDS1 shows about 20% lower conversion in comparison to the SDIDS2 and SDIDS3. $R_p$ for SDIDS1 is about 21% and 27% lower than their amounts for SDIDS2 and SDIDS3, respectively.

Samples removed at 180 and 270 minutes, within the interval II for all the three runs and also at 360 minutes in interval III for SDIDS3, were analyzed for the particle size which was further used to calculate the kinetic parameters such as $\bar{n}$, $N_p$ and $N_{pm}$. PSD curves (Fig. 2b) in accordance with SEM images (Fig. 3), clearly show that the particle sizes are biggest for SDIDS1, medium for SDIDS2 and the minimum for SDIDS3.

The $\bar{n}$ data in Table 4 show that the polymerization obeys Smith-Ewart kinetic case 3 with $\bar{n} > 0.5$ for SDIDS1 and case 1 with $\bar{n} < 0.5$ for SDIDS2 and SDIDS3 [40]. It also shows that $\bar{n}$ and $R_p / N_p$ increase by increasing the alcohol content in the SDIDS samples. For VCM, the average number of growing radicals per particle, $\bar{n}$, is reported to be much less than 0.5 [32, 33]. So, the radical desorption from polymer particles into the water phase is, thus, important [3, 41]. The results in Table 4 indicate that $\bar{n}$ shows agreement with its reported value in literature for SDIDS2 and SDIDS3. However, for SDIDS1, where the size of particles is bigger, $\bar{n}$ is higher due to lower radical desorption from polymer particles into the water phase [1].

Increase in $\bar{n}$ with increasing of alcohol content means that alcohol content influences the mass transfer phenomena. The probable reason that explains the decrease in free radical desorption by increasing of alcohol content might be related to the size of particles. The higher size of particles cause the decrease in desorption rate of free radicals from the particle phase. When particles’ diameter increases with increase in alcohol content (with respect to decrease in $N_p$), the surface area per particle will decrease as a result for SDIDS1. This would cause the increase in entrance efficiency of radicals to each particle, where $\bar{n}$ increase. And also the high solubility and mobility of the newly formed monomeric radicals in media with rich alcohol content and more oligo-micelle formation promote in entrance efficiency.

Generally, the number of particles created is determined by the balance between the rate of nucleation and the rate of coagulation [25]. Noteworthy that lower $N_p$ and $N_{pm}$ for SDIDS1 in comparison to the other two at 180 minutes have shown lower number of particles initiated at nucleation period in interval I. It seems emulsifier molecules in SDIDS1 does not have the ability to form spate of micelles in the alcohol dominant media which are qualified for particle nucleation [17, 18, 20].

Also significant reduction of $N_{pm}$ for SDIDS1 in comparison to the other two in conversion range of 32 to 50% at growth stage at in interval II is a sign for observing coagulation at higher rates in comparison to nucleation, leading to a drop in both $N_p$ and $N_{pm}$ which will end to an increase in
particle size. It is known that the formation of primary particles by homogenous nucleation during polymerization favors the growth of particles via association of small and large particles. The primary particles are colloidally unstable due to shortage of free emulsifiers which are being used for oligo-micelle formation. Hence they undergo coagulation with large polymer particles and polymerize very slowly [1]. Coalescence of particles increases the particle size and decreases the particle concentration. On the other hand, a drop in the number of particles simultaneously contributes to a slower overall reaction rate, \( R_p \) and higher polymerization rate per particle, \( R_p/N_p \) [29, 30] (Table 4). It could be concluded that SDIDS1 with higher alcohol content potentially has higher mobility (Table 3) at the equal mass concentration in comparison with SDIDS2 and SDIDS3. It manipulates more coagulation as a result, by the higher collision of the particles.

For SDIDS2, from conversion 37 to 71%, the reduction in \( N_p \) is less than its amount in SDIDS1 and also \( N_p \) is increased. This increase in \( N_p \) indicates the appearance of new particles [5]. It means that both coagulation and nucleation have happened simultaneously. But for SDIDS3, from conversion 35 to 69%, the \( N_p \) and \( N_p \) is increased with a higher rate in comparison with SDIDS2. This indicates that the nucleation rate is higher and very low coagulation is formed which is supported by lower particle size for SDIDS3. By considering similar alcohol contents for both SDIDS2 and SDIDS3 (Tab. 2), the difference in \( N_p \) and \( N_p \) for these two samples could be related to higher anion and lower water contents in SDIDS3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SDIDS1</th>
<th>SDIDS2</th>
<th>SDIDS3</th>
</tr>
</thead>
<tbody>
<tr>
<td>% ( X_{ov} ) final (a)</td>
<td>74.65</td>
<td>94.44</td>
<td>95.48</td>
</tr>
<tr>
<td>( dX_{ov} (t)/dt ) [min(^{-1})×1E-3]</td>
<td>2.34</td>
<td>2.83</td>
<td>3.00</td>
</tr>
<tr>
<td>( R_p ) [mol L(^{-1}) s(^{-1})×1E4]</td>
<td>4.94</td>
<td>5.98</td>
<td>6.31</td>
</tr>
<tr>
<td>Time [min]</td>
<td>180</td>
<td>270</td>
<td>180</td>
</tr>
<tr>
<td>% ( X_{ov} ) (t)</td>
<td>32.47</td>
<td>50.30</td>
<td>36.59</td>
</tr>
<tr>
<td>( d_{w} ) [nm]</td>
<td>316</td>
<td>386</td>
<td>247</td>
</tr>
<tr>
<td>( d_{pol} ) [nm]</td>
<td>377</td>
<td>461</td>
<td>295</td>
</tr>
<tr>
<td>( N_p ) [per liter aqueous phase] × 1E-16</td>
<td>0.66</td>
<td>0.56</td>
<td>1.57</td>
</tr>
<tr>
<td>( \tilde{n} )</td>
<td>0.728</td>
<td>0.856</td>
<td>0.373</td>
</tr>
<tr>
<td>( N_{pm} ) [per g polymer] × 1E-13</td>
<td>4.39</td>
<td>2.40</td>
<td>9.14</td>
</tr>
<tr>
<td>( R_p/N_p ) [mol s(^{-1})×1E20]</td>
<td>7.45</td>
<td>8.76</td>
<td>3.88</td>
</tr>
<tr>
<td>K-value</td>
<td>68.1</td>
<td>67.5</td>
<td>66.7</td>
</tr>
</tbody>
</table>

Coarse matter (a) [% wt]

<table>
<thead>
<tr>
<th>Coarse matter (a) [% wt]</th>
<th>Over (b)</th>
<th>Medium (c)</th>
<th>Nil (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(more than 10 % wt)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(about 2 - 5 % wt)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(less than 0.05 % wt)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) At the final conversion
(b) Runaway observed at this run
(c) Available due to very low coarse matter content
K-value quantities in Table 4 show that polymer chains can grow more for SDIDS1 in comparison to the small particles of SDIDS2 and SDIDS3 because the higher particle sizes reduce radical desorption rate from particles. Generally, desorption events are very operative in small particles while the formation of occluded or buried radicals or the fraction of less reactive radicals is more operative in large particles [1]. It is observed that $R_p / N_p$ and $\bar{n}$ increase with increasing $\bar{a}_{pwar}$ (Table 4) which is consistent with classical emulsion polymerization kinetics. It is expected that for SDIDS sample with higher alcohol content, diameter of polymer particles and the polymerization rate per particle increase with increasing the mobility of SDIDS monomers due to the higher oligo-micelle formation. Our results indicates that alcohol content has higher effect on particle growth ($R_p / N_p$) with inverse effect on the nucleation process and the particle number.

**Particle Growth History**

Fig. 2c compare PSD of SDIDS3 latexes removed at different time intervals. The PSD at time 180 minutes shows almost a skewed bell type distribution and two distinguished districts of particle sizes. The first district is very low in size distribution almost 75 nm with a frequency of % 15.6. The second one which is the main peak at almost 125 nm with a frequency of % 33.7. The PSD at time 270 minutes shows one main bell type curve with its peak shifting about 25 nm to higher particle sizes relative to the main peak of PSD at time 180 minutes. The interesting point is that the increase in the average particle sizes has been occurred by the cost of vanishing the smaller particles peak at 75 nm, and finally a small peak at 550 nm has formed. The PSD at time 360 minutes shows a distinguish district in size as skewness at 75 nm with a frequency of % 11.4 which confirmed the new particle formation. At higher particle size, the PSD curve is shifted to higher sizes around 475 nm which could be under the effect of coagulation at high conversions [5]. By the cost of formation of high particle sizes, the $N_p$ decrease and the condition would prepare for secondary particle formation [25]. It seems the condition of oligo-micelle formation could vary particle growth history. Generally, according to the emulsion polymerization theory, the number of particles remains constant after the interval I for VCM [2, 3] unless if the conditions change toward particle coagulation [23] or secondary particle formation [25]. Due to $N_{pm}$ quantities in Table 4, an optimized number of latex particles per unit mass of the polymer equal to $5 \times 1E$ 13 particles is assumed as a criterion $N_{pm}$ for a normal emulsion polymerization of VCM latex in the current study where, it is almost obtained for SDIDS1 at 180, for SDIDS2 at 270 and for SDIDS3 at time 360 minutes of the reaction times, respectively. Fig. 2d compare the PSD curves of the mentioned times for the three samples. Almost, similar trends with the least difference in particle sizes are obtained. It could be observed that the criterion particle growths are formed with a delay time from SDIDS1 to SDIDS3. The observed
behavior match with the trends observed for isopropyl alcohol content which promotes oligo-micelle formation, while an opposite trend is observed for anion content which promotes micelle formation from SDIDS1 to SDIDS3 (Table 1). It could be concluded that different condition of oligo-micelle formation would lead to different particle growth history.

**Figure 3.** SEM images (with scale bar 500 nm) of the three SDIDS samples at 270 minutes of polymerization.

**Latex Stability**

Latex stability for the polymerization used SDIDS1 could not exceed more than 75% conversion. The main parameter is thought to be responsible for this observation is believed to be the high concentration of alcohol. As discussed earlier when alcohol concentration is high, size of particles increases while the number of particles decreases. In this condition, termination reaction rate decrease while at the same time the viscosity in the particles increase due to a decreases in the value of $\dot{\mathbf{C}}_{\text{MP}}$ [3, 4]. Another possibility is the decrease in radical desorption rate from particles by promoting the polymerization auto- acceleration rate [7] which is observed as experimentally runaway. Also, the big coarse particles are settled as a separated phase at the reactor bottom. However, in the case of the other two samples, it was possible to convert VCM to $X_{\text{ov}}(t)$ up to about 95% due to their regular particle contents.

SDIDS3 with more anions and less isopropyl alcohol contents shows the highest stability with the least % wt coarse matter among the three studied samples. Although SDIDS2 in nearly all the parameters behave more similar to SDIDS3, however, the main reason for the differences in coagulation behavior and coarse matter content for these two samples are not exactly understood. Although due to results from Table 1, higher anion content of SDIDS3 seems to provide conditions leading to more coverage of the particles. Higher isodecyl alcohol content (0.6 %wt from Table 1) of SDIDS3, is believed to act as a nonionic emulsifier and increase the stability of emulsion system by decreasing the repulsion forces between the hydrophilic parts of the emulsifier [8, 21, 37-39].

In addition, the pH of the reaction media as a witness to track electrolyte change remained approximately unchanged all the times at around 7 during the polymerization course for all three runs.
However, when a runaway occurred (batch SDIDS1), a reduction in pH of the end aliquot was observed from 7 to 3–4 as an exception which probably related to PVC degradation, leading to the hydrochloric acid formation.

CONCLUSION

It was revealed that isopropyl alcohol content as co-solvent in the three SDIDS samples effect distinctly on their performances. In the series of studied samples, the highest isopropyl alcohol concentration and the lowest anionic content in the SDIDS samples (i.e., the sample SDIDS1) might be the reasons for the following observations:

1- Sooner and better promotion potential for oligo-micelles formation due to higher isopropyl alcohol content
2- Greater particle size due to the lower particle nucleation after the disappearance of the micellar emulsifier (end of the interval I)
3- Higher particle growth rate (\(\bar{n}\) and \(R_p/\bar{N}_p\)) due to an increase in the particle size and the emulsifier mobility which results in the step-like behavior
4- Slower overall rate due to the lower \(\bar{N}_p\) and its reduction by the coalescence of particles because of less strength of latex stabilization
5- Higher chain growth rate (K-value) due to the greater particle size and particle growth rate (\(\bar{n}\) and \(R_p/\bar{N}_p\)).

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REFERENCES


SYMBOLS AND ABBREVIATION

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>( C_E )</td>
<td>concentration of emulsifier in water</td>
</tr>
<tr>
<td>( C_{MP} )</td>
<td>overall monomer concentration in the polymer particles at interval II</td>
</tr>
<tr>
<td>( \dot{C}_{MP} )</td>
<td>overall monomer concentration in the polymer particles at interval III</td>
</tr>
<tr>
<td>( C_{M,0} )</td>
<td>initial monomer concentration (moles per unit volume of the continuous phase)</td>
</tr>
<tr>
<td>( d_i )</td>
<td>diameter of particle with index i.</td>
</tr>
<tr>
<td>( \bar{d}_{swol} )</td>
<td>particles diameter swelled with the monomer</td>
</tr>
<tr>
<td>( \bar{d}_v )</td>
<td>volume average particle diameter</td>
</tr>
<tr>
<td>( K_p )</td>
<td>coefficient of propagation rate</td>
</tr>
<tr>
<td>K-value</td>
<td>a measure of molecular weight for PVC</td>
</tr>
<tr>
<td>( M_M )</td>
<td>molecular weight of the monomer</td>
</tr>
</tbody>
</table>
M/W  weight ratio of monomer to water
$\bar{n}$  average number of growing chain per particle
$n_i$  number of particles with diameter $d_i$
$N_p$  number of latex particles per unit volume of the aqueous phase
$N_{pm}$  number of latex particles per unit mass of the polymer
$N_{av}$  Avogadro’s number
P/W  weight ratio of polymer to water
$R_p$  polymerization rate per unit volume of the continuous phase
$SC$  solid content
$SC_{(initial)}$  solid content at the beginning of reaction
$SC_{(final)}$  solid content at the end of reaction
$SC(t)$  solid content at time $t$
$X_c$  critical conversion
$X_{ov}(t)$  overall mass conversion at time $t$

Greek symbols
$\kappa$  conductivity
$\rho_P$  average density of the polymer
$\rho_W$  density of water
$\rho_M$  density of monomer
$\theta(t)$  overall molar conversion at time $t$

Abbreviations
CMC  critical micelle concentration
CMC$_L$  first minimum of CMC region
CMC$_H$  first maximum of CMC region
DM water  demineralized water
E-PVC  PVC produced by emulsion polymerization
K-value  a measure of molecular weight for PVC
PSD  particle size distribution
PVC  poly (vinyl chloride)
SDBS  sodium dodecylbenzenesulfonate
SDIDS  sodium di-isodecyl sulfoisuccinate
SDS  sodium dodecyl sulfate
SEM  scanning electron microscopy
SPS  sodium pentadecan- sulfonate
VCM  vinyl chloride monomer