Fluorescence spectroscopy and imaging of dynamics and microstructure of acrylic polymer emulsions

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Chapter 4

Redistribution of Texanol Among Latices of Different Composition

Cross Co-solvent Partitioning

Abstract

Repartitioning of co-solvent Texanol was observed in blends of latices having different co-polymers and $T_g$s. Hydrophobic latices (styrene-co-ethyl hexyl acrylate; S/EHA) and hydrophilic latices (methyl methacrylate-co-ethylacrylate; MMA/EA) were employed in these experiments. Steady-state fluorescence spectroscopy was used to monitor the repartitioning of Texanol.

Repartitioning of Texanol was found to be very rapid when it occurred from the low $T_g$ latex irrespective of the nature of the co-polymer. In high $T_g$ latices the repartitioning of Texanol was somewhat slower but still occurred within an hour. The final distribution of Texanol over the different polymer phases was found to be practically independent of the $T_g$ and the chemical composition of the co-polymers. The Hansen Solubility Parameter (HSP) values of Texanol are closer to those of PMMA than to those of PS, but our observation is that Texanol has almost similar affinity for hydrophobic and hydrophilic co-polymers.
4.1 Introduction

To understand how the use of coalescents in aqueous coatings can be optimized, it is very important to have knowledge of the partitioning of co-solvents between the aqueous and polymer phases in latex materials. In latex formulations co-solvents diffuse into latex particles, soften the polymer and lower its $T_g$. Plasticization of the polymer depends upon the concentration of co-solvent in the polymeric phase. As we have shown in the preceding chapters the concentration of co-solvent in latex particles can be effectively studied using fluorescence spectroscopy.

In Chapter 3 we have described the co-solvent repartitioning of various types of co-solvents ranging from moderate to fair water solubility in low and high $T_g$ hydrophilic and hydrophobic latices. These studies were performed in the bulk latex. A co-polymerized solvatochromic and fluorogenic fluorescent probe (Maleimidofluorotrope; MFT) was used to estimate the amount of co-solvents in latices via the changes in the maximum wavelength and the intensity of its emission. Repartitioning of co-solvents was found to be very fast in low $T_g$ latices. The order of the rate of co-solvent repartitioning was as follows:

Low $T_g$ hydrophilic = low $T_g$ hydrophobic >> high $T_g$ hydrophilic > high $T_g$ hydrophobic

In this chapter we applied the same concept and methodology as described in Chapter 3. In Chapter 3 the co-solvent repartitioning was studied between particles of the same latex. In this Chapter these studies were further elaborated to investigate the repartitioning of co-solvent when different co-polymer latices were mixed, which can be described as Cross Co-solvent Partitioning (CCP).

It is worth mentioning that the co-solvent repartitioning experiments (Chapter 3) and the cross co-solvent repartitioning experiments (Chapter 4) differ in two respects. Firstly, in Chapter 3 emulsions of similar composition and $T_g$ were mixed. In this Chapter, however, in one experiment four emulsions with entirely different composition and $T_g$ were combined. Secondly, the repartitioning of four different co-solvents - namely EEH, Texanol, DPnB and EEA - was reported in Chapter 3. In Chapter 4 only repartitioning of Texanol was studied.

Latices employed in the study were hydrophilic MMA/EA and hydrophobic S/EHA $T_g$ 20 and 60 °C latices. The emulsion polymerization recipe for the preparation of these materials and method of formulation of these latices is described in detail in Chapter 2 and 3 and will not be repeated here. All latices contained 2 wt-% acrylic acid (AA). It was added during emulsion polymerization to keep the emulsion stable. The emulsion polymerization was designed in such a way to obtain the final $T_g$ of ca. 20 and 60 °C for low and high $T_g$ latices, respectively. Theoretical $T_g$s were 20 and 60 °C but experimentally
observed values were slightly higher than these. The physical characterization of these latices is given in Chapter 2. For the sake of simplicity we will use the code of the latex showing its composition and $T_g$, e.g., S/EHA20 stands for S/EHA latex with predicted of $T_g$ 20°C.

In the present studies ten experiments were performed, subdivided into three sets, which were based on different combinations of latices. In one set of experiments similar co-polymer latices were blended, the difference being only in their $T_g$s. For instance S/EHA20 was mixed with S/EHA60 and in another experiment MMA/EA20 was blended with MMA/EA60.

In another set of experiments repartitioning of Texanol was studied when blending latices that differ in composition as well as in their $T_g$s. Four combinations of low and high $T_g$ hydrophilic and hydrophobic latices were prepared. For example S/EHA20 was mixed with MMA/EA60 in one experiment, and MMA/EA20 was blended with S/EHA60 in another.

The last set of experiments consisted of monitoring Texanol repartitioning in blends made only by the two high $T_g$ latices.

### 4.2 Cross Co-solvent Repartitioning Experiment

Based on the co-solvent repartitioning scheme, illustrated in the previous Chapter, various combinations of latices were designed. These combinations are discussed in each experiment in the Results and Discussion section. Figure 1 shows the cross co-solvent partitioning scheme, which combines two latices that differ from each other in chemical composition or $T_g$ of the material. These emulsions were mixed to get two blends. For a more extensive discussion of the co-solvent repartitioning scheme, the reader is referred to Chapter 3. For the sake of clarity the cross co-solvent partitioning scheme for each experiment is presented before the results.

Briefly about the co-solvent repartitioning experiment: four emulsions were prepared to perform one experiment. Emulsion I consisted of non-dye labeled latex containing co-solvent and emulsion III contained neither fluorescent label nor co-solvent. Emulsions II and IV both comprised the fluorescent label, the former without and the latter with the co-solvent. In the cross co-solvent repartitioning experiments discussed in this Chapter emulsions II and IV consisted of the same co-polymer composition. The emission maximum of the fluorescent label attached to the polymer not containing co-solvent (emulsion II) shifted to longer wavelengths (bathochromic shift) when formulated latex was added. This happened in blend 1 obtained by the mixing of emulsions I and II. When formulated dye-copolymerized latex was diluted with the non-labeled and non-formulated...
latex, this resulted in a hypsochromic shift in blend 2 that was the combination of emulsion III and IV.

Figure 1. Cross co-solvent repartitioning scheme: big circles, red small dots and green color represent latex particles, fluorescent label and co-solvent Texanol, respectively. Emulsion I and III were nonlabeled latex particles. Emulsions II and IV were fluorescently labeled latex particles. Emulsion II fluoresces at shorter wavelength because it contains no co-solvent. Emulsion IV was at longer wavelength due to the presence of co-solvent. Mixing of emulsion I and II was performed to obtain blend 1. Mixing of emulsions III and IV was done to get blend 2.

4.3 Results and Discussion

Repartitioning of the co-solvent Texanol was investigated in low and high \( T_g \) S/EHA and MMA/EA latices comprising 2 wt-% of acrylic acid. According to the co-solvent repartitioning scheme shown in Figure 1 two emulsions out of four contained co-solvent, i.e., emulsions I and IV. In all experiments emulsions I and IV were formulated with 9 % w/w Texanol, which was the only co-solvent studied in the present experiments. A solvatochromic fluorescent probe, Maleimidofluorotrope MFT was covalently linked to the co-polymer latices via emulsion polymerisation.\(^2\)\(^-\)\(^5\)

Co-solvent repartitioning was monitored using steady-state fluorescence spectroscopy. The emission measurements were started immediately after mixing equal amounts of the two latex emulsions in a quartz cuvet. For each experiment two blends were formed and emission spectra of each blend were measured for one hour during which twenty-one spectra were obtained. Integration time of each measurement was 100 sec. Fluorescence emission spectra obtained in this study were fitted with a skewed Gaussian function (see Chapter 2, section 2.2.1).\(^6\) The emission maxima obtained from the fluorescence spectra were further plotted against time to see the repartitioning behavior of Texanol.
A set of ten experiments in total were performed, as shown in Table 1. CCPn is the code used for the cross co-solvent partitioning experiment number n. Cross (×) and circle (○) in Table 1 present the experiments described in Chapter 3 and those not performed, respectively. It is worth mentioning that all experiments listed in Table 1 were performed twice to check the reproducibility and they provided similar results.

Table 1. List of cross co-solvent partitioning (CCP) experiments described in this Chapter.

<table>
<thead>
<tr>
<th>Non labeled latices</th>
<th>Fluorescently labeled latices</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MMA/EA20</td>
</tr>
<tr>
<td>MMA/EA20</td>
<td>×</td>
</tr>
<tr>
<td>MMA/EA60</td>
<td></td>
</tr>
<tr>
<td>S/EHA20</td>
<td>○</td>
</tr>
<tr>
<td>S/EHA60</td>
<td></td>
</tr>
</tbody>
</table>

× : experiments described in Chapter 3.
○ : experiments not performed.

The ten experiments shown in Table 1 were classified further in three sets by making various combinations of latices based on co-polymers and $T_g$s. Each of them will be explained under separate headings in the next sections.

In the experiments described in chapter 3, identical latices were blended, so that at equilibrium an equal distribution of the co-solvent over the labeled and nonlabeled latices is expected, corresponding to a 4.5% w/w concentration of the co-solvent in the fluorescent latex.

In the experiments described here, the co-solvent may have a different affinity for the two polymers involved, which would lead to an unequal distribution. In the two complementary experiments (blends 1 and 2), the label is in polymers with the same chemical composition, so the two blends should give the same ultimate emission wavelength.

### 4.3.1 Blending of Hydrophilic Latices

The latices used in this first set of experiments were the hydrophilic MMA/EA latex materials with low and high $T_g$. Two experiments were performed in this category, CCP1 and CCP2.
Figure 2. Steady-state fluorescence spectra of blends of MMA/EA $T_g$ 20 and 60 °C latices; A) CCP1, B) CCP2. Spectra of emulsion II and IV were measured once. For blends 1 and 2 spectra were measured for 1 hour. $\lambda_{exc} = 380$ nm.

In CCP1 emulsions I and III were made up of low $T_g$ latex and emulsions II and IV were made up of high $T_g$ MMA/EA latex. In CCP2, which was the reverse of CCP1, emulsions I and III were made up of high and emulsion II and IV were made up of low $T_g$ MMA/EA.
latices. Emulsion I and IV were formulated with the 9 % w/w Texanol. In Figure 3 the combinations are further visualized.

Figure 2 presents fluorescence emission spectra of both experiments measured for one hour after the blend formation. Each experiment consisted of 21 measurements: 21 for the hypsochromic and 21 for the bathochromic shifts. Emission maxima were obtained by fitting the spectra with the skewed Gaussian function (Chapter 2, section 2.2.1) and plotted against time, shown in Figure 3.

Blend 1 was formed by mixing emulsions I and II, which exhibited a bathochromic shift due to the migration of Texanol into the fluorescently labeled particles. Mixing of emulsion III and IV produced blend 2 which showed a hypsochromic shift as a result of migration of Texanol out of the fluorescently labeled latex particles. Cross co-solvent partitioning (CCP) scheme for each experiment is shown above the emission maximum versus time plots in Figure 3.

In CCP1 (Figure 2A) emission maxima of the non-formulated emulsion II and Texanol formulated emulsion IV were observed at 467 and 478 nm, respectively. Blends 1 and 2 showed the expected bathochromic and hypsochromic shifts, respectively (Figure 3A). Approximately after 5 minutes of blending both shifts coincided at 472 nm, the average of \( \lambda_{\text{max}} \) of emulsions II and IV.

In CCP2, Figure 2B, emulsion II and IV were made up of low \( T_g \) MMA/EA latex, whose emission maxima were at 478 nm and 495 nm, respectively. After 1 h blends 1 and 2 were observed at two different emission wavelengths, 482 and 489 nm, respectively. Assuming an equal distribution, the curves should have met at a peak maximum of 487 nm.

Repartitioning of Texanol was rapid in the first case (CCP1) when emulsion II and IV were made up of high \( T_g \) MMA/EA latex. Equilibrium was reached in ca. 5 min. In CCP2 it was slower and repartitioning of Texanol occurred in ca. 20 min. However, an equilibrium peak position that was the same for both blends was not reached within the time period of measurement, i.e., 1 h.

### 4.3.2 Blending of Hydrophobic Latices

Combinations of latices in this category consisted of only hydrophobic latices and they were mixed in the same way as hydrophilic latices described in the Section 4.3.1. Two experiments were performed, CCP3 and CCP4: in the former emulsion II and IV consisted of high \( T_g \) S/EHA and in the latter both these emulsions were made up of low \( T_g \) S/EHA latices. Fluorescence emission spectra are shown in Figure 4.
Figure 4. Steady-state fluorescence spectra of blends of S/EHA $T_g$ 20 and 60 °C latices; A) CCP3, B) CCP4. Spectra of emulsion II and IV were measured once and for blends 1 and 2 measured for 1 hour. $\lambda_{exc} = 380$ nm.

Figure 5. Emission maximum versus time plots for the blends of S/EHA $T_g$ 20 and 60 °C latices formulated with Texanol A) CCP3: fluorescent label was present in S/EHA $T_g$ 60 °C. Emulsion I and III were S/EHA $T_g$ 20 °C and emulsion II and IV were S/EHA $T_g$ 60 °C, B) CCP4: fluorescent label was present in S/EHA $T_g$ 20 °C. Emulsion I and III were S/EHA $T_g$ 60 °C and emulsion II and IV were S/EHA $T_g$ 20 °C.

In CCP3, Figure 4A, emulsions I, III and II, IV consisted of low and high $T_g$ S/EHA latices, respectively. The emission maxima of the non-formulated emulsion II and Texanol formulated emulsion IV were observed at 448 nm and 460 nm, respectively. In CCP4, Figure 4B, emulsions II and IV were made up of low $T_g$ S/EHA latex, whose emission
maxima were at 449 nm and 470 nm, respectively.

Figure 5 presents the emission maxima versus time plots for CCP3 and CCP4. In the former case, after 40 min of blending hypsochromic and bathochromic shifts coincided at 454 nm at the average of $\lambda_{\text{max}}$ of emulsions II and IV. Like hydrophilic latex partitioning of Texanol was rapid in this case (Figure 5A). In CCP4, surprisingly, fluorescence maxima of both blends remained ca. 10 nm apart, i.e., at 453 nm and 463 nm, respectively. Repartitioning of Texanol was slow when emulsions II and IV consisted of low $T_g$ S/EHA latices (Figure 5B). Blends 1 and 2 did not show convergence at a common equilibration point. Assuming an equal distribution, the curves should have met at a peak maximum of 460 nm.

### 4.3.3 Blending of Low and High $T_g$ Different Copolymer Latices

In this section those experiments will be discussed in which blends were prepared from emulsions of different co-polymers and different $T_g$s. In one case high $T_g$ hydrophilic latices were blended with low $T_g$ hydrophobic latices and vice versa (CCP5 and CCP6). In two more experiments high $T_g$ hydrophobic latices were mixed with low $T_g$ hydrophilic latices and vice versa (CCP7 and CCP8). In total four experiments were performed in this category.

The first two experiments of this section, namely CCP5 and CCP6, were performed by mixing fluorescently labeled hydrophilic latex with the nonlabeled hydrophobic latex. Figure 6 presents the fluorescence emission spectra of these two experiments.

Emulsions II and IV in CCP5 (Figure 6A) were observed at 465 nm and 477 nm respectively. In second experiment CCP6 (Figure 6B) emulsions II and IV were observed at 476 nm and 495 nm, respectively. Repartitioning of the co-solvent can be seen in the emission versus time plots of blends 1 and 2 for both experiments in Figure 7. In CCP5 bathochromic and hypsochromic shifts of blends 1 and 2 headed towards a common equilibration point within an hour and exhibited emission maxima at 470 nm and 471 nm, respectively (Figure 7A). Assuming an equal distribution of coalescent, a value of 471 nm would have been expected. In experiment CCP6, migration of Texanol was observed by the shift of emission of blends 1 and 2 by the bathochromic and hypsochromic shifts of blends 1 at 474 nm and blend 2 at 481 nm, respectively. However, the plot of the emission maxima showed rather erratic behavior, and the band maxima did not converge on a common equilibration point (Figure 7B). The expected average peak maximum for equal partitioning in this case was 486 nm.
Figure 6. Steady-state fluorescence spectra of MMA/EA with S/EHA latices; A) CCP5: emulsions II and IV were high $T_g$ MMA/EA latex, B) CCP6: emulsions II and IV were low $T_g$ MMA/EA latices. Spectra of emulsions II and IV were measured once and for blends 1 and 2 measured for 1 hour. $\lambda_{exc} = 380$ nm.

Figure 7. Emission maximum versus time plots for blends of MMA/EA and S/EHA $T_g$ 20 and 60 °C latices formulated with Texanol A) CCP5: fluorescent label was present in MMA/EA $T_g$ 60 °C. Emulsions I and III were S/EHA $T_g$ 20 °C and emulsions II and IV were MMA/EA $T_g$ 60 °C, B) CCP6: fluorescent label was present in MMA/EA $T_g$ 20 °C. Emulsions I and III were S/EHA $T_g$ 60 °C and emulsions II and IV were MMA/E $T_g$ 20 °C.
Figure 8. Steady-state fluorescence spectra of MMA/EA with S/EHA latices; A) CCP7: emulsions II and IV were high $T_g$ S/EHA latex, B) CCP8: emulsions II and IV were low $T_g$ S/EHA latices. Spectra of Emulsions II and IV were measured once and for blends 1 and 2 measured for 1 hour. $\lambda_{exc} = 380$ nm.

Figure 9. Emission maximum versus time plots for blends of MMA/EA and S/EHA $T_g$ 20 and 60 °C latices formulated with Texanol A) CCP7: fluorescent label was present in S/EHA $T_g$ 60 °C. Emulsions I and III were MMA/EA $T_g$ 20 °C and Emulsions II and IV were S/EHA $T_g$ 60 °C, B) CCP8: fluorescent label was present in S/EHA $T_g$ 20 °C. Emulsions I and III were MMA/EA $T_g$ 60 °C and Emulsions II and IV were S/EHA $T_g$ 20 °C.

Two further experiments of this series, CCP7 and CCP8, were those in which emulsions II and IV comprised S/EHA co-polymers. Fluorescence emission spectra of these experiments are shown in Figure 8. In experiment CCP7 emission maxima of emulsion II...
and IV (S/EHA $T_g$ 60 °C) were observed at 448 nm and 460 nm, respectively (Figure 7A). In CCP8 the starting emulsions (S/EHA $T_g$ 20 °C) exhibited emission maxima at 449 nm and 470 nm, respectively (Figure 8B).

Figure 9 shows the emission maxima versus time plot for experiments CCP7 and CCP8. In CCP7 experiment blends 1 and 2 showed a shift of emission maxima towards an essentially constant value but did not meet at a common wavelength within an hour and they remained at 454 nm and 457 nm, respectively (Figure 9A). Assuming an equal distribution of Texanol, the expected peak maximum was 454 nm. A similar situation was observed in experiment CCP8 (Figure 9B) where blends 1 and 2 showed emission maxima at 457 nm and 459 nm, respectively. Theoretically, the average peak maximum would have been expected at 460 nm.

### 4.3.4 Blending of High $T_g$ Latices

The experiments described in this section were those in which the blending of high $T_g$ hydrophobic and hydrophilic latices was studied. Two experiments were performed: in the first case (CCP9) emulsions I and III were made up of high $T_g$ hydrophobic latex and emulsions II and IV were high $T_g$ hydrophilic latex, whereas in the second case (CCP10) this combination was reversed.

Figure 10 presents the fluorescence emission spectra of experiments CCP9 and CCP10. In CCP9 S/EHA $T_g$ 60 °C was blended with MMA/EA $T_g$ 60 °C. Emulsions II and IV were dye labeled latices of high $T_g$ MMA/EA latex, they were observed at 465 and 478 nm, respectively. Repartitioning of Texanol occurred gradually: hypsochromic and bathochromic shifts showed almost complete convergence at a common emission maximum, i.e., 470 nm around 60 min of blend formation (Figure 11A). The final peak maximum was expected at 472 nm.

Fluorescence emission spectra of CCP10 are presented in Figure 10B. Here emulsions II and IV comprised high $T_g$ S/EHA copolymers and they were observed at 448 and 460 nm, respectively. Migration of Texanol was observed by hypsochromic and bathochromic shifts, although equilibration at a common wavelength was not observed. Blend 1 and Blend 2 remained at 452 and 456 nm, respectively (Figure 11B). For equal distribution of Texanol over the polymer phases, this value should have been 454 nm.
Figure 10. Steady-state fluorescence spectra of blends of high $T_g$ MMA/EA with S/EHA latices; A) CCP9: emulsions II and IV were high $T_g$ MMA/EA latex, B) CCP10: emulsions II and IV were high $T_g$ S/EHA latices. Spectra of emulsions II and IV were measured once and for blends 1 and 2 measured for 1 hour. $\lambda_{exc} = 380$ nm.

Figure 11. Emission maximum versus time plots for blends of MMA/EA and S/EHA $T_g$ 60 °C latices formulated with Texanol A) CCP9: fluorescent label was present in MMA/EA $T_g$ 60 °C. Emulsions I and III were S/EHA $T_g$ 60 °C and emulsions II and IV were MMA/EA $T_g$ 60 °C, B) CCP10: fluorescent label was present in S/EHA $T_g$ 60 °C. Emulsions I and III were MMA/EA $T_g$ 60 °C and emulsions II and IV were S/EHA $T_g$ 60 °C.
4.4 Discussion

Repartitioning behavior of Texanol was observed in hydrophilic and hydrophobic latices when mixed in various ways. In experiments where all four emulsions were either hydrophilic (4.3.1) or hydrophobic latices (4.3.2) the repartitioning behavior of Texanol was found to be similar, i.e., when the fluorescently labeled emulsions II and IV were high \( T_g \), a rapid repartitioning was observed, but when these two emulsions were low \( T_g \), repartitioning occurred at a lower rate and did not lead to the expected coincidence of the emission maxima in the complementary experiments. In these experiments emulsions I and IV were formulated ones, in which the actual \( T_g \) of the latex particles was low due to the presence of co-solvent in it. Escape of co-solvent from such a latex (hypsochromic shift) was very rapid when it consisted of low \( T_g \) polymer and somewhat slower in the case of high \( T_g \) latex, as seen when comparing Figure 3A with 3B and Figure 5A with 5B. When emulsion I was made up of low \( T_g \) latex (CCP1, CCP3) it quickly released Texanol, which entered in the more viscous high \( T_g \) particles of fluorescently labeled Emulsion II, resulting in a bathochromic shift. Likewise, a low \( T_g \) emulsion III quickly absorbed co-solvent and coincidence of emission maxima of hypsochromic and bathochromic shifts of blends was observed at a common wavelength.

On the other hand when emulsions I and III were made up of high \( T_g \) latex (CCP2, CCP4), release of Texanol was relatively slow. In these experiments, the emission maxima of the probes in the labeled emulsions did not undergo the complete shifts to the average values within an hour. Especially the bathochromic shifts were smaller than expected. The reason for this is unclear at present. Possibly, there are slow components in the repartitioning process in some cases. This issue is left to future investigations.

In the second set of experiments where four emulsions in one experiment consisted of different co-polymers and different \( T_g \)s, diverse results were obtained. The first case was different from the remaining three. A rapid repartitioning of Texanol was observed in the experiment where fluorescently labeled emulsions II and IV were high \( T_g \) MMA/EA latex (CCP5, Figure 7). In the remaining three experiments both hypsochromic and bathochromic shifts showed migration of Texanol but they did not exhibit a common equilibration point.

Only in CCP5 equilibration occurred at the expected equilibration point (471 nm). In CCP6 behavior was somewhat erratic. Possibly, Texanol has a preference for the hydrophobic phase, because the hypsochromic shift “overshoots” and the bathochromic shift does not clearly occur. In CCP7 the equilibration point for equal partitioning was 454 nm. The bathochromic shifts led to this “equilibrium” value and the hypsochromic shift was incomplete. The difference, however, was only 3 nm. This might suggest a slight
preference of Texanol for the hydrophobic latex. In CCP8 the equilibration point was 460 nm. The hypsochromic shift was faster than the bathochromic shift and here Texanol seems to have small preference for the high $T_g$ material.

In third set of experiments where only high $T_g$ latices were blended, repartitioning of Texanol was observed in both situations when escape and entry of Texanol occurred from S/EHA or MMA/EA latices. However, escape of Texanol from MMA/EA latex (emulsion IV in CCP9) was much faster than from the S/EHA latex (emulsion IV in CCP10). Entry of co-solvent occurred at a relatively slow rate in both experiments. The affinity of the co-solvent Texanol might be higher for the hydrophobic latex than for the hydrophilic latex.

Generally, in these experiments one should not expect to find the equilibration point for blends 1 and 2 at a point corresponding to an equal fraction of co-solvent in both polymers, especially in cases when emulsions were different with respect to the chemical structure of the co-polymers and $T_g$s. The results presented here, unexpectedly, strongly suggest that neither $T_g$ nor chemical composition of polymer strongly affects the thermodynamic equilibria of the Texanol in latex blends. There might be a slight preference for Texanol to soften the high $T_g$ particles rather than the low $T_g$ particles, and a small preference for the hydrophobic phase, but the preferences are weak in any case. In other words, the partitioning coefficient of Texanol over two chemically different polymers appears to be remarkably close to 1.

A coalescent is a vital component of a paint formulation to obtain a high quality film.\textsuperscript{7, 8} Due to the slow evaporating ability of a coalescing agent it swells the latex particles and softens them to lower the minimum film formation temperature. Texanol is known as an excellent coalescing aid for poly vinyl acetate latices, acrylic homopolymer latices, styrene/acrylic copolymer latices, etcetera.\textsuperscript{9, 10} In our experiment of detection of Texanol repartitioning we have observed that in entirely different compositions the repartitioning behavior of Texanol was quite similar. It showed a quick repartitioning in styrene based hydrophobic latex as well as highly polar methyl methacrylate based hydrophilic latex material. However, in the hydrophilic latex it was faster than in the hydrophobic one.

Texanol is moderately soluble in water (858 mg/L at 20 °C) and the log $P_{o/w}$ (octanol/water) value of Texanol is 3.47.\textsuperscript{11} These values show that Texanol is likely to be in the polymeric phase of the latex. Our observations agree with this and our results show that Texanol is not very selective for the composition of the material, it efficiently and equally partitioned in hydrophobic as well as hydrophilic co-polymers.

Texanol exhibited a dual character, it was found to be as good a co-solvent in hydrophobic as in hydrophilic co-polymers.\textsuperscript{9} Our results show that the affinity of Texanol for different
polymers is very similar. A commonly used approach to estimate the compatibility of a co-solvent with that of a co-polymer is to compare the Hansen solubility parameters (HSP). Materials having similar Hansen solubility parameters (HSP) have a high affinity for each other.\textsuperscript{12} It is based on the rule “like dissolves like”: solvents with similar HSP values are miscible to a large extent. The solubility parameter (\(\delta\)) proposed by Hansen is the sum of three parameters: dispersion (\(\delta_D\)), polar (\(\delta_P\)) and hydrogen bonding (\(\delta_H\)) (Equation 1).

\[
\delta = \delta_D + \delta_P + \delta_H
\]  

(1)

The HSP values of pure solvents are measured via the heat of vaporization. For polymers and high boiling point substances experimental measurement of the heat of vaporization is not possible. Alternatively, the use of HSP values of monomers is a common practice.\textsuperscript{13} Lewin et al. predicted the HSP values acrylate monomers and found close resemblance of experimental and predicted values.\textsuperscript{14}

Table 2 presents the HSP (\(\delta\)) values for the monomers used, for the homopolymers polystyrene and PMMA, and Texanol. The values of HSP for Texanol are obtained from data sheets given by the provider.\textsuperscript{15}

<table>
<thead>
<tr>
<th>Material</th>
<th>Hansen solubility parameter (\delta) (cal/cm(^3))(^{1/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\delta_D)</td>
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<td>MMA</td>
<td>7.7</td>
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<td>EA</td>
<td>7.6</td>
</tr>
<tr>
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<tr>
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</tr>
<tr>
<td>PS</td>
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</table>

The individual values of solubility parameters of Texanol most closely resemble those of MMA and EA monomers, but our results definitely show that it is nearly equally compatible with all four co-polymers used. The low polarity of Texanol favors interaction with the hydrophobic materials, the hydrogen bonding that with the acrylic esters. The large differences in the HSP values for the homopolymers and the corresponding monomers makes it questionable to predict the distribution of Texanol based on the available HSP values.
4.5 Conclusion

Repartitioning behavior of Texanol was monitored as a function of time in various combinations of low and high $T_g$ hydrophobic S/EHA and hydrophilic MMA/EA acrylic latices. In low $T_g$ hydrophilic and hydrophobic latices the repartitioning was very fast and in high $T_g$ latices it occurred at comparatively slower rate. Experiments were performed twice to check the reproducibility and similar results were found in both attempts. We infer that the thermodynamic equilibrium distribution of Texanol in latices is almost independent of the composition and the $T_g$ of the materials. Still more experiments are needed to be done on a variety of materials to gather more data to have a global view. Different polymers such as polyurethanes, alkyds, and others can be a possible extension of this study. The application of the simple method developed here to the investigation of more solvents having low, moderate and high water solubilites may open a new horizon of information on the repartitioning of these solvents.

4.6 Experimental details

4.6.1 Co-solvents and Formulations

Texanol (2,2,4-trimethyl-1,3-pentanediol(2-methylpropanoate)), was the only co-solvent used in the experiments described in this Chapter. In the co-solvent partitioning experiments, formulated fractions of latex contained 9 % w/w Texanol. The pH of latex as prepared (see Chapter 2) was raised to 7 – 7.5 using ammonia. Next, the coalescing agent was added slowly with continuous stirring by a mechanical stirrer over 30 min to produce a stable formulation. To prepare 100 g of 9 % w/w Texanol formulated S/EHA latex, 9 g of Texanol was slowly added to 91 g of S/EHA latex at pH 7.

4.6.2 Blend formation

Blend formation is explained in Chapter 3. Briefly, 1 ml of each emulsion (i.e., emulsion I and II or emulsion III and IV) was added into the quartz cuvet and the whole amount was sucked once in and out of the pipette to ensure the thorough mixing of the two emulsions. Emission measurement was started within a minute after blending and emission spectra were recorded for one hour. The acquisition of each spectrum (200 points, 0.5 s/point) took 100 seconds. The amounts of latex added and temperature (room temperature or the heat generated during mixing) have very little or negligible effect on the fluorescence of the MFT probe (Chapter 3). Each experiment was repeated twice to ensure the reproducibility and repetition produced similar results.
4.7 References

11. Screening Information Data Sheet (SIDS) of 2,2,4-Trimethyl-1,3-Pentanediol Monoisobutyrate (Texanol). 1994, Organisation for Economic Co-operation and Development (OECD). High Production Volume Chemicals Programme, USA.
15. Material Safety Data Sheet (MSDS) of Texanol. 2005, Eastman Chemical Company USA.