Partitioning of Monobutyl Itaconate and β-Carboxyethyl Acrylate Between Organic and Water Phases

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ABSTRACT: Unsaturated carboxylic acids are usually used as functional monomers at low concentrations in emulsion polymerization to improve the colloidal stability and the mechanical properties of the films prepared from the corresponding latexes. These acids are distributed between the aqueous and organic phases to different extents due to their various water solubilities. The partitioning behavior of two new vinyl acids, monobutyl itaconate (MBI) and β-carboxyethyl acrylate (β-CEA), between n-butyl methacrylate (BMA) and the water phases was studied in this work. In addition, the partitioning of commonly used acrylic acid (AA) and methacrylic acid (MAA) was also determined as a benchmark. It was found that the partition coefficients (D) of MBI and β-CEA depended to a large extent on the acid concentration in the total comonomer mixture; the same trends were observed for AA and MAA. With the variation in monomer to water ratio (M/W), the D value of lipophilic acid MBI changed significantly, while for hydrophilic acid β-CEA, the D value changed very little. Furthermore, the values of the partition coefficient of MBI and β-CEA were very strong functions of pH, decreasing rapidly as the pH is increased. On the other hand, temperature has little effect on the partition coefficients for vinyl acids under typical emulsion polymerization reaction conditions. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40868.

INTRODUCTION

Carboxylated copolymer latexes are often synthesized by emulsion polymerization via the addition of a small amount of functional carboxylic acid in the comonomer mixture. These latexes are typically used in the production of textile, coatings, and adhesives.[1] The application of unsaturated carboxylic acids as functional comonomers at low concentrations (usually < 20 wt % of the total monomer) in emulsion polymerization is well known. Although these vinyl acids are partially or completely soluble in water, they will still partition to varying extents into the organic phase depending on their relative hydrophobicities. The most frequently studied acid monomers used in emulsion polymerization are itaconic acid (IA),[2,3] acrylic acid (AA),[4,5] methacrylic acid (MAA),[5,6] and fumaric acid (FA),[2] listed in order of their hydrophobicities.

In the present study, we employed two new unsaturated monocarboxylic acids, monobutyl itaconate (MBI) and β-carboxyethyl acrylate (β-CEA), in the emulsion polymerization

of n-butyl methacrylate and compared their behavior to the two most widely used acid monomers (AA and MAA). IA esters are obtained by introducing one or two ester groups in the molecular structure of IA. In addition, the monoesters were found to be more active in polymerization than the corresponding diesters and IA and therefore play an important role in the synthesis of a variety of polymers and copolymers such as adhesive, cleaning media, surfactants, and plastic additives, etc,[7–9] with free carboxyl groups that offer improved properties. Significant results obtained by copolymerizing monoitaconates are a possibility of balancing hydrophilic/hydrophobic properties at different pH levels.[10] Lu et al.[11] discussed the function of three different carboxylic monomers in acrylate emulsion copolymerization, and found that the latex prepared with MBI has better water resistance than latex with AA. Hence, monoitaconate esters, especially MBI which contains both ester and carboxylic groups, are in high market demand. β-CEA is a carboxylic monomer of the acrylic or MAA type. A significant difference of β-CEA compared to common carboxylic acids is the greater
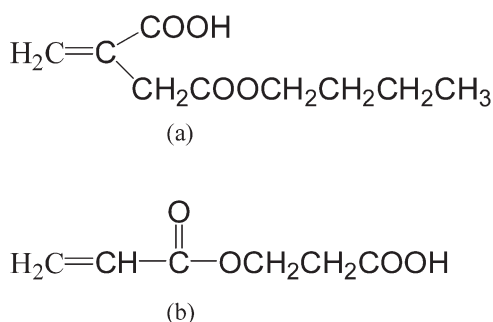
Scheme 1. The molecular structures of (a) MBI and (b) β-CEA.

separation of the carboxylic acid functional group from the unsaturated vinyl functionality in the molecule. It can be polymerized in solution or emulsion to produce acrylic, vinyl-acrylic, or styrenic-acrylic polymers with improved adhesive properties. Other major characteristics of β-CEA monomer are: (1) it promotes flexibility in the copolymers owing to the relative low glass transition temperature (T_g) of its homo-polymers(<30°C). (2) It provides improved adhesion and stability to the emulsion polymers, due to its —COOH groups being more available than those in the conventional carboxylic acids. (3) β-CEA can be incorporated into the copolymer at high levels over a wide pH range, due to its more reactive salt form compared to AA. (4) β-CEA is more compatible with other monomers, hence reducing polymerization in the aqueous phase and producing more uniform copolymers because of its long chain.[12]

Although a few fundamental studies have been carried out concerning the behavior of MBI[11,13] and β-CEA[14] in emulsion polymerizations, the distribution of these two new functional monomers between the organic and aqueous phases has not been investigated until now. The partitioning behavior of the carboxylic acids between the organic and aqueous phases depends on many factors such as temperature, pH, composition, type, and concentration of surfactant, etc.[6] Since many significant aspects of the emulsion polymerization process depend on the partitioning behavior of the (co)monomers, such as the rate of reaction and the carboxyl groups distribution, it is important to have a quantitative understanding of the partitioning behavior of different carboxylic acids between oil and water phases.

In this article, partitioning of MBI and β-CEA between butyl methacrylate and the water phase will be studied by examining the influence of changes in the acid concentration in the total monomer mix, pH, temperature, and the mass ratio of monomer to water (M/W) on the value of partitioning coefficient (D) in a system comprised of the monomers (butyl methacrylate and carboxylic acids) and water. These results are compared to those obtained using the more common acrylic (AA) and methacrylic (MAA) acids.

EXPERIMENTAL

The monomers used in this study are AA (Alfa Aesar), MAA (Sigma Aldrich), MBI (TCI America), β-CEA (β-CEA; Sigma

Aldrich), and n-butyl methacrylate (BMA; Acros Organics). All monomers were used as received. Phenolphthalein indicator (RICCA Chemical), sodium hydroxide (NaOH; Acros Organic), hydrochloric acid (HCl; VWR), and hydroquinone (HQ; Alfa Aesar) were used as received. All experiments were carried out with deionized water with resistivity of 18.2 MΩ cm and TOC (total organic carbon) levels as low as 1 ppb. The molecular structures of MBI and β-CEA are shown in Scheme 1.

The individual vinyl acids (dissolved in water) and butyl methacrylate (BMA) were prepared in 300-mL glass beakers and stirred for 30 min with a magnetic stirrer (Fisher). The overall concentration of carboxylic acids was varied within the range of 1–20% by weight of the total monomer. Afterwards, the monomer–water mixtures (the mass ratio of monomer to water ranged from 0.25 to 1.5) were added into a separatory funnel and allowed to equilibrate for 60 min. After that, thermodynamic equilibrium conditions were assumed to exist. About 20 mL of water phase were then collected by slow draining through the bottom of the separatory funnel for analysis.

For the experiments designed to study the effect of pH, a $2M$ aqueous solution of NaOH was used to adjust the pH of the initial acidic aqueous solution, after separation of the two phases, $1M$ aqueous solution of HCl was used to bring the pH of the water phase to 3 (to associate vinyl acids).

The experiments at higher temperatures were carried out in a 500 mL four-neck round-bottom flask equipped with an electronic stirrer, thermometer, and reflux condenser. Experiments were performed at 50 and 70°C, with 500–600 ppm hydroquinone solution (5 wt %) present in the aqueous phase to avoid polymerization. The agitation speed was then kept constant for 30 min. Then, the agitation was stopped and the system was allowed to equilibrate for an additional 60 min in the temperature-controlled bath. After this, 20 mL of the water phase was withdrawn from the bottom of the reactor flask using a disposable pipette for analysis.

Partition coefficients of the unsaturated carboxylic acids between the organic phase and the aqueous phase were determined through acid–base titrations with $0.1M$ aqueous solution of NaOH. The analyses were performed with a pH meter (HACH sensION+ pH3), also using 2 droplets of a 0.5% (wt/vol) phenolphthalein solution (prepared in alcohol 50% vol/vol) as a visual indicator of the neutralization point. To increase the

Table I. pKa Values for Vinyl Acids Used in this Work

Carboxylic acid	pK_a[a]	pK_a (reported in other literature)	pH (1 g/100 mL)[a]
AA	4.23	4.23,[4] 4.25[15]	2.55
MAA	4.49	4.45,[4] 4.36,[16] 4.65[17]	2.72
MBI	4.20	no data	2.74
β-CEA	4.99	no data	3.08

[a] This work.

Table II. Effect of Acid Concentration in the Total Monomers on the Partition Coefficient

Carboxylic concentration (wt %)	Partition coefficient			
	AA	MAA	MBI	β-CEA
1	0.450 ± 0.046	2.67 ± 0.110	11.23 ± 0.086	0.908
3	0.595 ± 0.017	3.26 ± 0.108	14.77 ± 0.046	1.04 ± 0.035
5	0.653 ± 0.020	3.69 ± 0.050	18.44 ± 0.318	1.13
10	0.762 ± 0.007	4.69 ± 0.099	19.27	1.25 ± 0.029
20	1.044 ± 0.065	6.35 ± 0.023	24.10 ± 0.248	1.48 ± 0.023

precision of the experimental measurements, titrations were performed three times at each particular experimental condition.

The partition coefficient (D) of the carboxylic monomer between BMA and the water phase is defined as the ratio of the acid concentration in the organic phase ($C_{o,tot}$) to the acid concentration in the aqueous phase ($C_{w,tot}$)[6]:

$$D = \frac{C_{o,tot}}{C_{w,tot}} \quad (1)$$

The pH of the acid aqueous solution was determined with a pH meter, and pK_a values for the vinyl acids were calculated as follows:

$$[H^+] = 10^{-pH} \quad (2)$$

$$K_a = \frac{[H^+][A^-]}{[HA]_o - [H^+]} = \frac{[H^+]^2}{[HA]_o - [H^+]} \quad (3)$$

where $[HA]_o$ is the total concentration of the acid monomer.

$$pK_a = -\log_{10} K_a \quad (4)$$

RESULTS AND DISCUSSION

Acidity Comparison of the Four Kinds of Carboxylic Acid Monomers

The pH and pK_a values for these four different carboxylic acids measured in this work are reported in Table I.

It can be seen that the pK_a values of AA and MAA are consistent with the results reported in other literature. However, the pK_a values of the new carboxylic monomers MBI and β-CEA are not found in any other documents. MBI is a solid-state and lipophilic carboxylic acid monomer; a small amount can be dis-

solved into water in the form of oil droplets. Furthermore, its pK_a value was nearly the same as AAs and MAAs. This similarity was primarily caused by the similar molecular structure for these three acid monomers, i.e., the -COOH group is directly attached to an unsaturated vinyl group. In the case of β-CEA, a different behavior was observed. It is of interest to comment that although β-CEA is a very hydrophilic acid, the acidity of the acid solution was the weakest among the four acid monomers that were studied, based on the pK_a values listed in Table I. As we know, the unsaturated vinyl functionality attached to the carboxyl group would enhance the acidity of the carboxylic acid due to its electron-withdrawing inductive effect. Also note that the strength of the inductive effect produced by unsaturated vinyl group is dependent on its position within the carboxylic acid structure. The further from the site of ionization, the lower the inductive effect. So β-CEA is a "weaker" acid when compared with the other three acids due to its greater separation of the carboxylic acid functional group from the polymerizable vinyl functionality, resulting in its highest pK_a value.

Effect of Acid Concentration in the Total Monomers on the Partition Coefficient

The effect of acid concentration in the total monomer mixture on the partition coefficients are shown in Table II. The ratio of monomer to water (M/W) was 1 : 3 throughout the experiments in this part. The molecular interactions responsible for these variations are shown in Figures 1–3. There will be more discussion on this later.

Table II shows the partition coefficients of different carboxylic acids between BMA phase and the water phase. When the acid concentration in the total monomers is 3 wt %, we obtained partition coefficient values for AA and MAA between BMA and water at 25°C of 0.595 ± 0.017 and 3.26 ± 0.108, respectively. These values are in excellent agreement with reported values of
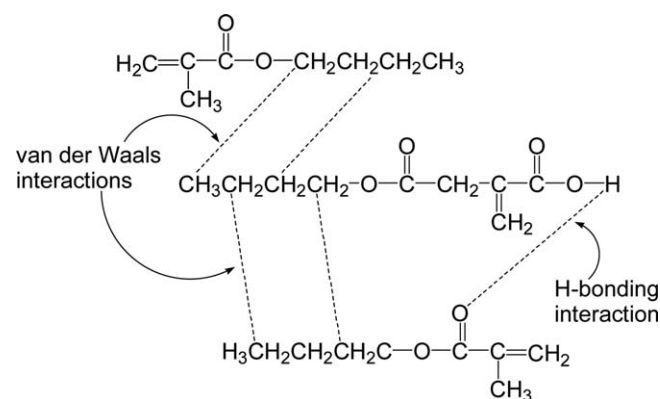

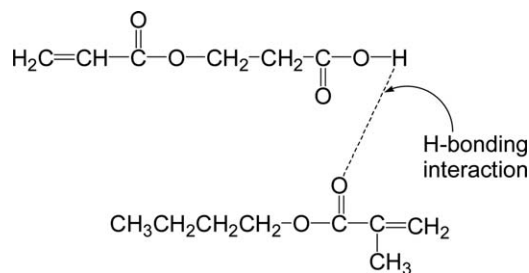**Figure 1.** Molecular interaction between MBI and BMA monomer.

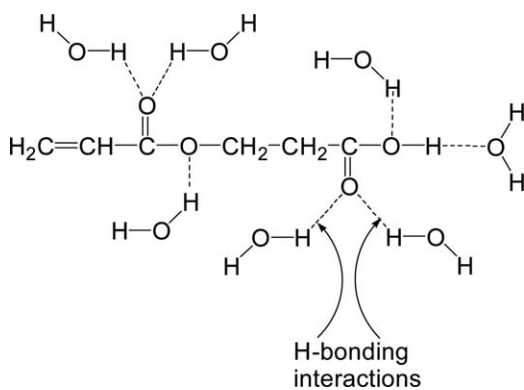**Figure 2.** Molecular interaction between β-CEA and BMA monomer.

Figure 3. Molecular interaction between β-CEA and water.

Figure 5. Acid concentration in the total monomers versus the aqueous phase ($C_{w,tot}$) at equilibrium at 25°C ($M/W = 1/3$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

0.580 ± 0.052[4] and 3.28 ± 0.124[4] for AA and MAA, respectively. The agreement also suggests that the method used in this work can effectively determine the distribution of carboxylic acids between water and organic phase.

Prausnitz et al.[18] note that dimerization of carboxylic acids is often observed in solvents by hydrogen bonding such as styrene. However, this may not occur when (meth)acrylic monomer is used as the organic phase. Tripathi and Sundberg[4] proposed that the presence of the carbonyl groups in the (meth)acrylic monomers results in an absence of dimerization in the organic phase, instead finding molecular interactions with the >C=O groups in the monomers shown in Figures 1 and 2.

From Table II, it can be seen that the partition coefficient of MBI is the largest among the four acid monomers due to its strongest lipophilicity. This is a result of MBI's ability to both H-bond with the polar carbonyl group, and participate in van der Waals interactions with the non-polar hydrocarbon functionality present in BMA as illustrated in Figure 1. On the other hand, β-CEA has a much lower partition coefficient when compared with MBI due to its hydrophilicity. However, it is interesting to point out here that β-CEA even has a lower D value than MAA. From Scheme 1, we can clearly see that β-CEA has a longer chain compared to MAA and meanwhile it is shown in Table I that its acidity and

ionization degree are weaker than MAAs. However, as a result of the ability to form more "solubilizing" H-bonding interactions with water due to the extra carbonyl group in its molecular structure as illustrated in Figure 3, β-CEA displays higher water solubility compared with MAA.

From Figures 4 and 5, we can see that as the initial acid concentration in the total monomers increased, the acid molar concentration in water phase ($C_{w,tot}$) linearly increased. The acid molar concentration in organic phase ($C_{o,tot}$) also increased. In conclusion, the partition coefficient for acid monomers increased with the acid concentration in the total monomers, and the values of the partition coefficient for these four different carboxylic acids between BMA and the water phase showed a decreasing order: $MBI > MAA > \beta\text{-CEA} > AA$, irrespective of the acid mass concentration in the total monomers.

Effect of the Ratio of Monomer to Water (M/W) on the Partition Coefficient

In this section, we discuss the effect of the monomer to water ratio (M/W) on the partition coefficient of MBI and β-CEA
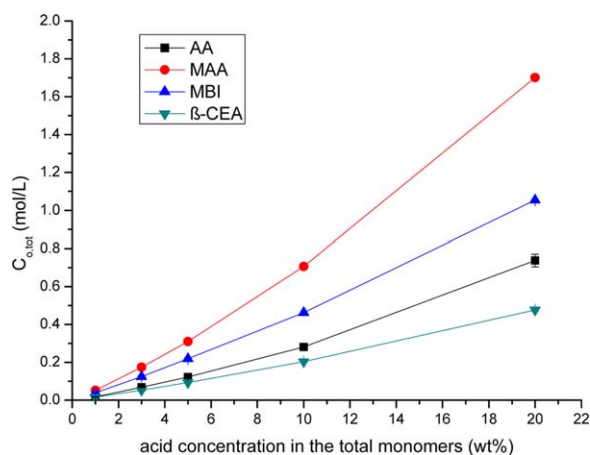

Figure 4. Acid concentration in the total monomers versus the organic phase ($C_{o,tot}$) at equilibrium at 25°C ($M/W = 1/3$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
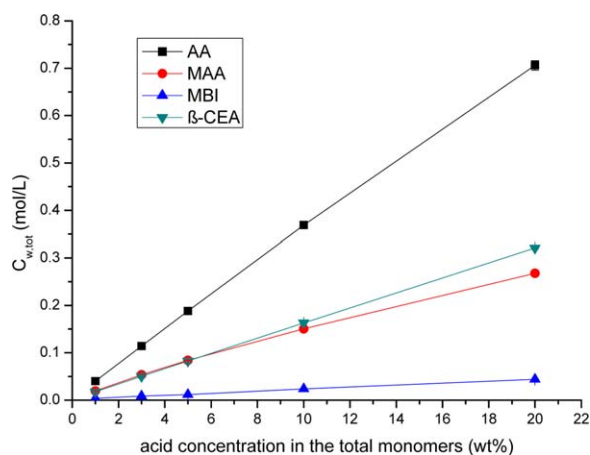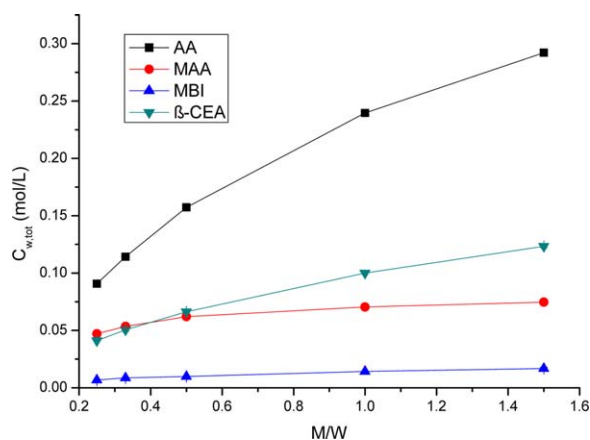

Figure 6. The ratio of monomer to water (M/W) versus the aqueous phase ($C_{w,tot}$) at equilibrium at 25°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
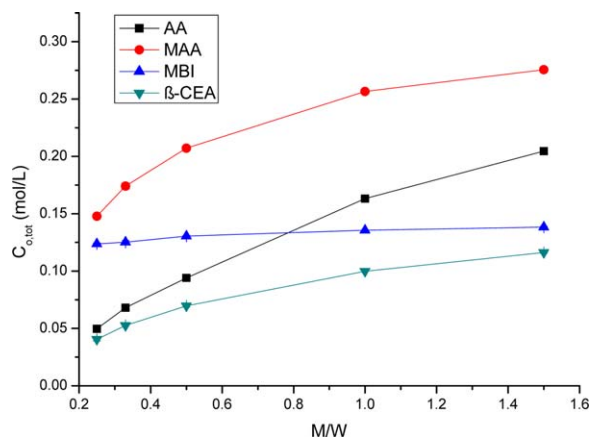
Figure 7. The ratio of monomer to water (M/W) versus the organic phase ($C_{o,tot}$) at equilibrium at 25°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

between the organic and aqueous phases. The acid concentration was 3% by weight of the total monomers and kept constant throughout the experiments.

As can be seen from Figure 6, it would appear that the monomer to water ratio (M/W) does not have a significant effect on $C_{w,tot}$ for MBI due to its very high hydrophobicity. On the other hand, when M/W is increased, the acid concentration in the organic phase after partitioning ($C_{o,tot}$) for MBI was nearly unchanged as shown in Figure 7. However, a different behavior was observed for the hydrophobic carboxylic acid MAA. This occurs because the MBI has a much higher hydrophobicity compared to MAA due to the interactions between BMA and MBI plotted in Figure 1, resulting in most of the MBI partitioning into the organic phase irrespective of the amount of water phase. This is also the reason that why M/W almost has no effect on $C_{w,tot}$ for MBI which was illustrated in Figure 6.

An earlier report[19] on the partitioning characteristics of AA between styrene and the water phase suggested that changes in M/W had very little effect on the fraction of AA distributed in the organic phase, but we find that not to be the case in our research system. In contrast to MBI, the $C_{o,tot}$ for hydrophilic acid β-CEA increased with increasing M/W, the same trend was observed for AA. This is an indication of the molecular interactions between the carbonyl group in the BMA monomer and the carboxyl group in the carboxylic acids listed in Figure 2.

Table III shows the partition coefficients for the four different kinds of carboxylic acid as a function of monomer to water weight ratio, M/W. In Table III, it is clear that the partition coefficient for MBI-BMA-water system is highly dependent on the monomer/water ratio (M/W). As described in the experimental details, the partition coefficient D is calculated from the measured $C_{w,tot}$ values and the $C_{o,tot}$ values determined from the mass balance. It can be seen from Figures 6 and 7 that $C_{o,tot}$ and $C_{w,tot}$ for MBI change very little with the increment in M/W. However, the increasing extent in $C_{w,tot}$ was larger than in $C_{o,tot}$, due to its very strong lipophilicity, resulting in the decreasing partition coefficient. In other words, little variations in $C_{o,tot}$ and $C_{w,tot}$ will be able to generate significant changes for the partition coefficient values of the strong lipophilic acid monomer, indicating that the larger the partition coefficient for carboxylic acid, the more sensitive it is to the variation of $C_{o,tot}$ and $C_{w,tot}$.

In contrast to MBI, the distribution of β-CEA between BMA and water phase is much lower, as shown clearly in Table III. These D values for β-CEA are an order of magnitude lower than those for MBI. This is of course because of the much more polar nature of the β-CEA. Besides, unlike MBI, the partition coefficient for β-CEA showed no dependency on M/W, the same trend we can see for AA, which may be caused by its high hydrophilicity. The interactions between the vinyl acids (MBI and β-CEA) with the oil phase (BMA) and water phase, respectively, are shown in Figures 1 and 2. These help us to understand that MBI and β-CEA behave differently in their inherent water and oil solubilities. For MAA, its partition coefficient values increased slightly with M/W which is in great agreement with those found in the literature.[20] This is totally different from MBI's behavior due to MAA's weaker lipophilicity compared with MBI.

Finally, we can conclude here that the ratio of monomer to water (M/W) does have a significant effect on the distribution of hydrophobic vinyl acids between the BMA and water phase due to the very large partition coefficient value, and the stronger the lipophilicity, the greater the effect. Nevertheless, the partition coefficient value for hydrophilic acid monomers was not greatly affected by M/W.

Effect of pH on the Partition Coefficient of Carboxylic Acids

Figures 8 and 9 show the effect of the pH on the distribution coefficient of MBI and β-CEA, respectively, between an organic phase, comprised of BMA, and the water phase. The acid

Table III. Effect of M/W on the Partition Coefficient of Carboxylic Acids

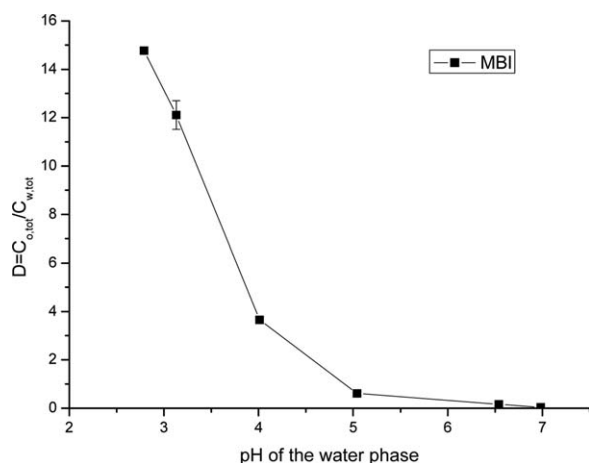|	Partition coefficient			
M/W	AA	MAA	MBI	β-CEA
1/4	0.548	3.14 ± 0.057	18.19 ± 0.566	0.98 ± 0.041
1/3	0.595 ± 0.017	3.26 ± 0.108	14.77 ± 0.046	1.04 ± 0.035
1/2	0.598 ± 0.009	3.34 ± 0.090	13.28 ± 0.450	1.05 ± 0.029
1/1	0.681 ± 0.010	3.64 ± 0.046	9.47	1.00
3/2	0.700	3.69 ± 0.058	8.33 ± 0.600	0.94 ± 0.017

Figure 8. Effect of pH on the partition coefficient of MBI between BMA and water phase.

concentration in the total monomer was 3 wt % and the ratio of monomer to water (M/W) was 1 : 3 throughout the experiments in this section. The shapes of the curves obtained in this study are the same as observed for the commonly used AA and MAA.[6,20] As shown in both figures, the pH plays a significant role in the value of the partition coefficient for carboxylic acid, where D decreases considerably as the pH is increased. This is mainly because that the negative charge on the dissociated form of the carboxylic acid (—COO$^-$) gives it a stronger polarity than the non-dissociated form of the acid (—COOH). The higher polarity of —COO$^-$ increases its attraction to the polar water molecules, and decreases its attraction to the relatively nonpolar molecules in the organic phase. So it can be seen from Figure 8, even though the MBI is a strongly lipophilic carboxylic acid, as the pH increases, its partition coefficient between organic and water phase decreases dramatically, and this trend holds until the pH reaches 7, at which point nearly all of the MBI is to be found in the aqueous phase. It is important to note here that most of the MBI was partitioned in the organic phase when the pH of the water phase was not changed, which further indicates that the pH is a determining factor in the value of the partition coefficient for MBI.
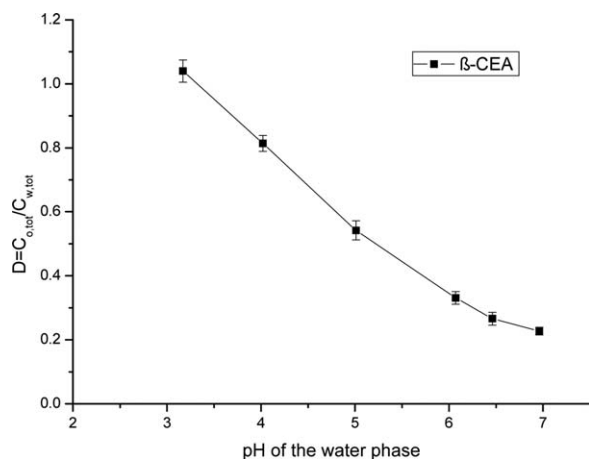

Figure 9. Effect of pH on the partition coefficient of β-CEA between BMA and water phase.

Table IV. Effect of Temperature on the Partition Coefficients of MBI and β-CEA

Temperature (°C)	Partition coefficient	
	MBI	β-CEA
25	14.77 ± 0.046	1.04 ± 0.035
50	12.99 ± 0.520	1.10 ± 0.029
70	14.87 ± 0.236	1.32 ± 0.063

However, for the hydrophilic carboxylic monomer β-CEA, its partition coefficient decreases linearly with increasing pH, as shown in Figure 9. Furthermore, when pH reaches 7, the overall fraction of β-CEA in the organic phase is more than MBIs. This may be explained by the observation that β-CEA is a "weaker" acid when compared with MBI, and its strong hydrophilicity primarily depends on the hydrogen-bond interactions between the carbonyl and carboxyl groups in the β-CEA molecule and water molecules as shown in Figure 3. Nevertheless, the hydrophilicity of the strong lipophilic acid MBI is primarily dependent on its degree of dissociation due to its more acidic nature when compared with β-CEA. So here we may conclude that the partition coefficient of the "strong" acid is more sensitive to pH, when compared with a "weak" acid, irrespective of the water solubility of the carboxylic acids.

Effect of Temperature on the Partition Coefficient
Emulsion polymerization reactions are usually conducted in the range of 55–85°C. In this work, we studied the effect of temperature on the partitioning of MBI and β-CEA between water and BMA monomer over a 25–70°C range.

From Table IV, it is clear that neither the partition coefficient values (D) of MBI nor β-CEA change dramatically over the 25–70°C range. This may be primarily due to the constant pK_a values for experiments carried out at temperatures other than 25°C. This assumption will not be far from reality as, first, the degree of ionization of the acid without addition of buffer or base is less than 3% when the acid level is >0.05 mol/L,[4] and, second, the change in pK_a values for weak acids with temperature is quite small.[21,22] In the meantime, Leo et al.[23] proposed that the effect of temperature on partition coefficient is not significant if the two phases are not very miscible with each other. Our results here are also consistent with the works of Tripathi and Sundberg[4] and Santos et al.[6]

The results obtained on the different partitioning behaviors for carboxylic acids between organic and water phases from this study are of great importance because they allow us to better understand the different carboxyl group distributions in latexes and derived films, and their resulting properties for our future works.

CONCLUSIONS

Several conclusions can be drawn from the experimental results presented in the current work:

1. MBI has similar pK_a value with AA and MAA. β-CEA is a "weaker" acid when compared with the other three acids due to its greater separation of the carboxylic acid

functional group from the polymerizable vinyl functionality, resulting in its highest pK_a value.

2. The partition coefficients of vinyl acids between BMA and the water phase are strongly affected by the acid concentration in the total monomers. Moreover, these four different carboxylic acids display a decreasing order in their D values: MBI > MAA > β-CEA > AA, irrespective of the acid mass concentration in the total monomers.

3. The monomer/water ratio (M/W) has a significant effect on the partition coefficient of hydrophobic vinyl acids between BMA and the water phase, and the stronger the lipophilicity, the greater the effect. Nevertheless, the partition coefficients for hydrophilic acid monomers are not strongly affected by M/W.

4. The partition coefficients for MBI and β-CEA are strongly influenced by variations in pH. It is argued that this is due to the affinity of the dissociated form of vinyl acids (which is found in higher concentrations as the pH increases) for water. Besides, the partition coefficient of the "strong" acid (MBI) is more sensitive to the pH, when compared with the "weak" acid (β-CEA), irrespective of the water solubility of the carboxylic acids.

5. The partition coefficients of vinyl acids appear to be independent of the temperature due to the small change in pK_a values for weak acids with temperature.

It should be noted here that we didn't study the effect of the initial acid concentration in the aqueous phase on the partition coefficient throughout the work like many other studies in the literature do. We are concerned more about the application of the partition coefficients to emulsion polymerization systems. Here our interests lie in how, (1) the acid concentration, based on monomers, and in the range of commonly used emulsion polymerization processes; (2) the mass ratio of monomer to water, emulating the different solids content of the emulsion polymers; (3) the different pH values, close to those used in buffering of emulsion polymerization reactions; (4) the different temperature of the emulsion polymerization processes, affect the partition coefficient for different kinds of carboxylic acids in the BMA and water phases. These research directions are more closely aligned to systems used in emulsion polymerization.

ACKNOWLEDGMENTS

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