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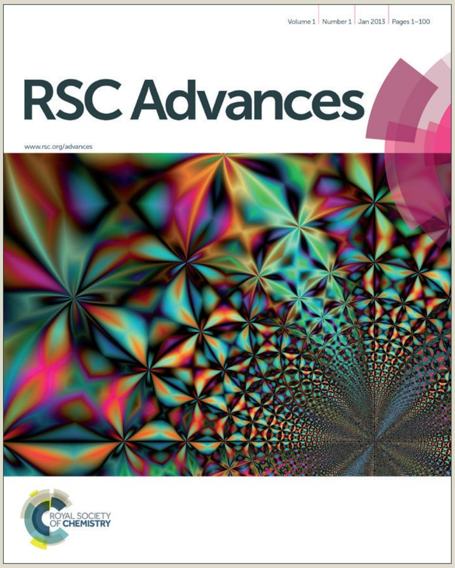

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Temperature-Dependent Oil Absorption of Poly(oxypropylene)amine-Intercalated Clays for Environmental Remediation

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The natural silicate clays with layered structure were intercalated by polyether-amines via ionic exchange reaction and subsequently applied for oil absorption. The polyether-amines including hydrophobic poly(oxypropylene)-amines (POP-amines) and the hydrophilic poly(oxyethylene)-amine (POE-amine) were used to intercalate sodium montmorillonite (MMT). The organoclays from POP-monoamine of 2,000 g/mol (POP-M2000) demonstrated the ability of absorbing petroleum crude oils in water at the efficacy of 15 times the weight of organoclay. Owing to the property of Lower Critical Aggregation Temperature (LCAT) at 50 °C, the organoclays absorbed oils and self-aggregated into oil lumps and phase separated out from water cleanly above the temperature. By comparison, a homogeneous emulsion-like dispersion was formed at low temperatures of 15 °C. This phenomenon was explained by the inherent property of Lower Critical Solubility Temperature (LCST) due to the presence of POP-organics intercalated in the clay galleries. Besides the POP hydrophobicity for high efficiency of oil absorption, the LCAT behavior rendered the easiness of oil recovery under heating. The oil-absorbed clay aggregates were analyzed by XRD showing the expansion and layer exfoliation of the clay structure during the oil incorporation. The understandings of their POP-intercalated and oil-absorbed tertiary structures led to the potential uses in the areas of secondary oil recovery, shale oil extraction and remedy of oil pollution in water.

1. Introduction

In the past, oil spill in ocean had occasionally occurred and has caused serious impacts on the shoreline environment.[1, 2] A wide range of methods and materials for oil-spill remediation including the uses of pickering emulsion technique,[3] absorbents,[4] superhydrophobic materials,[5, 6] and skimmers[7] have been reported. However, most of these methods are complicated in treating procedures and often time-consuming. The methods may have not enough efficiency for applying in a large scale of oil spills in ocean. In addition, the problem is often encountered for chemical incompatibility to the environment or the issues of harmfulness to the biological system. For example, in the disaster of the Gulf of Mexico oil spill happened in 2011, a large amount of chemical dispersants were sprayed from the air and injected into the deep-sea to dissipate oils. The concern of long-term effect on the deep-water ecosystem in that area is still debating.

In viewing the drawbacks of the conventional methods, we have utilized the naturally occurring silicate clays such as sodium montmorillonite (MMT) which are considered to be environmentally benign materials. Our previous work has demonstrated the feasibility of using poly(oxyalkylene)-polyamine salts for the clay intercalation in order to modify the water-swellable clay into amphiphilic properties.[8] Using the technique of organic intercalation, the layered structure of clay galleries were expanded and hosted with hydrophobic organics and becoming affinity for oil absorption. Our purpose of clay modification is different from the conventional organic intercalation for the applications such as catalysts,[9] adsorbents, and polymer nanocomposites.[10-12]

We have adopted the basics of clay chemistry including ionic exchange reaction and organic interaction with the high surface silicates.[13,14] Previously,[15] we have studied the modification of the silicate clays by poly(oxypropylene)amine-salts and secondarily encapsulated with iron-oxide nanoparticles (FeNPs). The possible incorporation of FeNPs in the nanostructure of layered silicates enabled the absorbed oils to be removable by simply applying a magnetic field. More recently, we found that the key step of hydrophobic intercalation in the clay galleries actually went through a stepwise mechanism, i.e. the first step of ionic exchange reaction with a critical concentration for spacing expansion and the second step of hydrophobic phase segregation in the layered structure.[8] The findings prompted us to further study and prepare the organically modified clays more suitable for oil applications.

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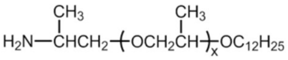
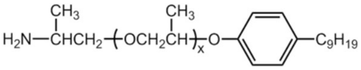
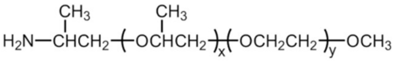
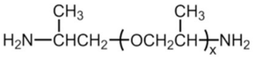
Table 1. Chemical structures of polyether-amines including POP- and POE-amines as the precursors for clay intercalation

Name	Chemical structure	Oxyethylene/oxypropylene ratio	Mw.	Solubility[a]	
				Water	Toluene
POP-M300	 $H_2N-\overset{CH_3}{CH}CH_2-(OCH_2\overset{CH_3}{CH})_x-OC_{12}H_{25}$	0/3	300	–	+
POP-M1000		0/14	1,000	–	+
POP-M2000	 $H_2N-\overset{CH_3}{CH}CH_2-(O\overset{CH_3}{CH}CH_2)_x-(OCH_2CH_2)_y-OCH_3$	6/29	2,000	–	+
POP-D2000	 $H_2N-\overset{CH_3}{CH}CH_2-(OCH_2\overset{CH_3}{CH})_x-NH_2$	0/33	2,000	–	+
POE-D2000	 $H_2N-\overset{CH_3}{CH}CH_2-(O\overset{CH_3}{CH}CH_2)_x-(OCH_2CH_2)_y-(OCH_2\overset{CH_3}{CH})_z-NH_2$	39/6	2,000	+	–

[a] + soluble; – insoluble at 10 wt% solubility tests in water or toluene.

In this work, a series of POP-intercalated silicate clays were compared for their ability of oil absorption. The hydrophobic and hydrophilic polyether-amines with different molecular weights were used to intercalate clay and also correlated the clay gallery expansion with oil-absorption ability. Most significantly, it was found that the POP-intercalated clays exhibited an intriguing temperature dependency in oil absorption. The oil-absorbing ability is not only related to the basal spacing expansion but also to their secondary unit aggregation or phase separation from the water. In other words, the unique property of Lower Critical Solubility Temperature (LCST) of POP-amines is shown in the POP/silicate organoclays, which exhibit the aggregation depending on the temperature owing to the disruption of hydrogen bonding of the POP segments in water. This temperature dependency occurring in clay-oil-water interactions could be used in the process of oil-water separation, secondary oil recovery, and shale oil extraction. More importantly, a promising use for the remediation of oil-contaminated water would be immediately expected.

2. Experimental section

2.1 Materials

One of the naturally occurring phyllosilicates, sodium montmorillonite (Na^+-MMT), comprising the generic structure of 2:1 tetrahedral and octahedral aluminosilicate sheet structure, was supplied by Nanocor Co. (USA). The clay minerals are aggregates of primary units in stacks. Each individual sheet has a dimension of approximately 100 x 100 x 1 nm^3 and 8–10 sheets in one primary stack in average.[16] The smectite clay with layered structure was estimated to have cationic exchange capacity (CEC) of 1.20 mequiv./g. In this capacity the organic ions may exchange with the counter metal ions such as Na^+ and other alkali metal ions (Mg^{2+}, Ca^{2+}, or Fe^{2+}). Both of hydrophobic and hydrophilic polyether-backboned amines were purchased from Huntsman Chemical Co. (USA). The molecular weight (Mw.) of hydrophobic poly(oxypropylene)- (POP-) monoamines with 300, 1,000, and 2,000 g/mol were abbreviated as POP-M300, POP-M1000, and POP-M2000, respectively. The POP-diamine of 2,000 g/mol Mw. was abbreviated as POP-D2000. Another type, the hydrophilic poly(oxyethylene)- (POE-) backboned diamine with 2,000 g/mol Mw. was a water-soluble amine and was abbreviated as POE-D2000. Their chemical structures of diamines and monoamines of various molecular weights were illustrated in Table 1.

2.2 Preparation of Organically Modified Clay

The family of POP- and POE-amines including POP-M300, POP-M1000, POP-M2000, POP-D2000, and POE-D2000 with different molecular weights were used for ionic exchange intercalation into the clay layered structure. These amines were acidified by titration with one equivalent amount of hydrochloric acid in water to generate the correspondent ⍰ $NH^{3+}Cl^-$ salts. The intercalation of MMT by using the HCl-treated POP- and POE-backboned polyether-amines has been reported previously.[8,10] In a typical procedure, MMT (10.0 g, 1.20 mequiv./g) was swelled in deionized water (800 mL) at 80 °C for 3 h. The amine salts were separately prepared by treating the amine with HCl in an acidification equivalent. An aliquot of the amine/HCl salt was added into the MMT slurry in a stoichiometric amount on the basis of the clay CEC (1.20 mequiv./g). The slurry was vigorously mixed by mechanical stirring at 80 °C for 0.5 h. The resultant precipitates were filtered, washed thoroughly with deionized water, and dried at 50 °C for 24 h. The organoclays were analyzed by X-ray powder diffraction and used as oil absorbents.

2.3 Determination of Lower Critical Aggregation Temperature (LCAT) for Organoclays

The organoclays, prepared from ionic exchange reaction of MMT, including POP-D2000/MMT, POE-D2000/MMT, and POP-M2000/MMT, were made into 0.1 wt% dispersion by magnetically stirring in water at 5 °C for 1 hr. The dispersions were placed in a quartz cell and measured the transmittance at the wavelength of 550 nm during the programmed ramping of temperature from 0 °C to 80 °C. Each measurement point was held one hour to reach equilibrium. When the temperature was increased, the original fine dispersion appeared to become turbidity and white precipitation. This aggregation phenomenon was found to be reversible as the temperature gradually decreasing. The aggregation temperature was recorded as Lower Critical Aggregation Temperature (LCAT). The corresponding Lower Critical Solubility Temperature (LCST) for POP-amines was measured in the same manner.

2.4 The Efficiency of Oil Absorption

A beaker (250 mL) equipped with a magnetic stirring bar was charged with petroleum crude oil/water (0.50 g/20 g) slurry and then organoclays (0.50 g) were added under the agitation at 15 °C for 30 min. The absorption efficiency was determined by incrementally adding oils into the clay slurry to observe its oil/clay aggregation and separated from water. The process of incremental addition of oil was continuously agitated and periodically changing the temperature between 15 °C and 50 °C after each oil addition. The temperature fluctuation was purposely performed to observe the LCAT phenomenon. Through this process, the oil absorption occurred gradually and the clay/oil aggregated and, in some cases, precipitated out in lumps from the water phase. Finally, a clear separation of oil from water was achieved. When the oil was not entirely separated from water then the addition amount of oil was defined as beyond absorption efficiency of organoclay. If the oil was absorbed by clay, the aggregation might not occur or only formation of oil/water slurry, and then it was defined as “none” of efficiency. A vivid illustration of oil/water separation by adding organoclay was recorded in a video (Electronic Supplementary Information movie)

2.5 Characterization

LCAT was determined by measuring the transmittance of organoclays at the wavelength of 550 nm through a programmed ramping of temperature from 0 °C to 80 °C by an UV-Vis spectrophotometer (V-570, Jasco). X-ray powder diffraction (XRD) was performed by using a PANalytical X’Pert PRO diffractometer with Cu target (k = 1.5408 Å) at a generator voltage of 45 kV and current of 40 mA to record the basal spacing (*d* spacing) of all clay samples. The pattern of basal spacing was calculated according to Bragg’s equation ($n\lambda = 2d\sin\theta$). The value for n = 1 was calculated from the observed values for the higher order of n such as n = 2, 3, 4, etc. by fitting the equation. The thermal analyses were measured by using a thermal gravimetric analyzer (TGA) (Perkin-Elmer Pyris 1 model). The organic fraction was calculated from the weight loss by programming the temperature from 100 °C to 800 °C at the rate of 10 °C/min.

3. Results and discussion

3.1 Intercalation of MMT with Polyether-Amine Salts

The organoclays were prepared by the intercalation of the multilayer-structured Na^+-MMT with the polyether-amine-salts. The hydrophobic POP-series and hydrophilic POE-series of amines were treated with hydrochloric acid to become amine-salts and then allowed the ionic exchange reaction with the clay. Accordingly, the family of organically modified clays including POP-M300/, POP-M1000/, POP-M2000/, POP-D2000/, and POE-D2000/MMT, were prepared from the five different polyether-amines (as structurally illustrated in Table 1). After intercalations at 1.0 equivalent ionic exchanging, the polyether-amine-salts were incorporated into the clay multilayered galleries and led to the expanded basal spacing (as shown by XRD *d* value). As a result, the *d* spacing of Na^+-MMT at 12 Å was expanded to 26 Å for POP- M300/MMT, 48 Å for POP-M1000/MMT, and 73 Å for POP-M2000/MMT, as recorded in Table 2. It was noted that the expansion of clay interlayer spacing was proportionally dependent on the end-to-end length or relatively the molecular weight of POP backbones in the trend of M2000 > M1000 > M300.[17] Further comparison to POP-D2000 diamine of the similar molecular weight at *d* spacing of 52 Å, the POP-M2000 monoamine gave a much higher spacing of 73 Å, under the same 1.0 CEC equivalent ratio. It is noteworthy that two POP-amines have similar POP molecular weight and incorporated into the layered silicate in similar weight fraction, 73 wt% versus 74 wt% of organics based on TGA. The difference in *d* spacing could be derived from the amine-salt termini in contacting with the silicate platelet surface. The POP backbone generated hydrophobic phase segregation in the clay interlayer galleries in different density for basal spacing expansion. In other words, the difference in the terminal structure between the mono- and the di-amine significantly generated different hydrophobic phase segregation. It implies that the correspondent organoclays had different hydrophobic affinity for oily organics. The hydrophobic effect is indirectly evidenced by the organoclays generated with the water-soluble POE-D2000 diamine of similar molecular weight but hydrophilic POE backbone, which intercalated at only 18 Å basal spacing, due to the lacking of hydrophobic phase segregation in the clay galleries and, as expected, none of oil affinity.

The selected POP-monoamine (POP-M2000) was further investigated for the details of clay intercalation with different ionic exchanging CEC equivalents. In our previous studies,[8] we reported that the intercalation of POP-monoamine into clay by stepwise mechanism for incorporating hydrophobic organics. The POP-M2000 can intercalate into clay spacing through the ionic exchange reaction in the first step, and continuously expand by the second mechanism of hydrophobic attraction of POP backbones. Hence, the intercalating organics in the second step are not required to be ionic species for ionic exchange reaction but the hydrophobic compounds for expanding the layered spacing. The second hydrophobic organics can further create more hydrophobic phase and the

Table 2. Performance and characterization of various organoclays for oil absorption

Intercalation agents	Amine/ clay (CEC)[a]	Intercalated organoclays		LCAT[c]	Oil added/ organoclay (w/w)	After oil absorption		Efficiency (absorbed oil/organoclay, w/w)[d]
		Organic fraction (wt%)[b]	*d* spacing (Å)			Organic fraction (wt%)[b]	*d* spacing, (Å)	
None (Na^+-MMT)	--	0	12	–	N. D.	N. D.	N. D.	None[e]
POP-M300	1.0	28	26	+	1/1	35	34	Up to 10/1
POP-M1000	1.0	57	48	+	1/1	73	60	Up to 12/1
POP-M2000	0.3	43	18	–	1/1	71	78	None
	0.5	50	72	–	1/1	77	88	None
	0.7	61	71	–	1/1	81	84	None
	1.0	73	73	+	0.1/1	76	84	0.1/1
					0.5/1	79	92	0.5/1
					1/1	82	95	1/1
					3/1	90	97	3/1
					5/1	92	111	5/1
					10/1	96	116	10/1
					15/1	98	N.D.	15/1
	2.0	82	84	+	1/1	85	103	Up to 15/1
	4.0	89	100	+	1/1	83	108	Up to 15/1
POP-D2000	0.3	36	17	–	1/1	69	18	None
	1.0	74	52	+	1/1	86	52	1/1
					2/1	91	51	2/1
					3/1	91	54	3/1
					5/1	94	52	5/1
					10/1	95	N.D.	10/1
POE-D2000	1.0	63	18	–	1/1	68	18	None

[a] equivalent ratio of amine-H^+ to MMT (CEC: cation exchange capacity, 120 mequiv./100 g)
[b] determined by TGA
[c] – : no LCAT was observed, +: LCAT was observed
[d] efficiency was calculated from equation (1) for the weight ratios of oil/organoclay, the endpoint was defined by the oil/clay aggregation and clear separation from water.
[e] none: no water/oil separation (due to lacking of LCAT of the clay)

expansion of clay galleries. The second step of hydrophobic intercalation implies the ability of the organoclays for accommodating oil absorption.

In order to understand the hydrophobic factor affecting the efficiency of oil absorbing, the organoclays of various organic fractions derived from POP-M2000 intercalation at 0.3, 0.5, 0.7, 1.0, 2.0 and 4.0 of equivalent ratio to the clay CEC were prepared. The XRD analyses showed different d values at 18, 72, 71, 73, 84 and 100 Å, respectively. There was a critical amount of POP-M2000 to clay CEC at the equivalent ratio of 0.5, the *d* spacing exhibited a sudden change from 12 Å to 72 Å. This demonstrated a critical amount of POP organics for generating the hydrophobic phase in the nanostructures. The hydrophobic phase would be formed by the methyl-POP backbone (i.e., POP-M2000 monoamine) aggregation when greater than 0.5 equivalent of POP intercalation. Afterwards, the multi-layered silicates can perform a further accommodation for the incoming hydrophobic organics in the second-stage intercalation, i.e. oil absorption.

3.2 Temperature-Dependent Aggregation of the Organoclays

As shown in Table 2, some of the organoclays have the temperature-dependent dispersion behaviours in water. Three polyether-amines, POP-M2000, POP-D2000, and POE-D2000, were examined for the property of Lower Critical Solubility Temperature (LCST) in the temperature range of 0–80 °C, as shown in Figure 1. By comparison, the solubility of hydrophobic POP-backboned amine is temperature-dependent while the POE-amine has the same solubility throughout the temperature rising up to 80 °C, without showing LCST property. The term of Lower Critical Aggregation Temperature (LCAT) is derived from the POP-intercalated organoclays which

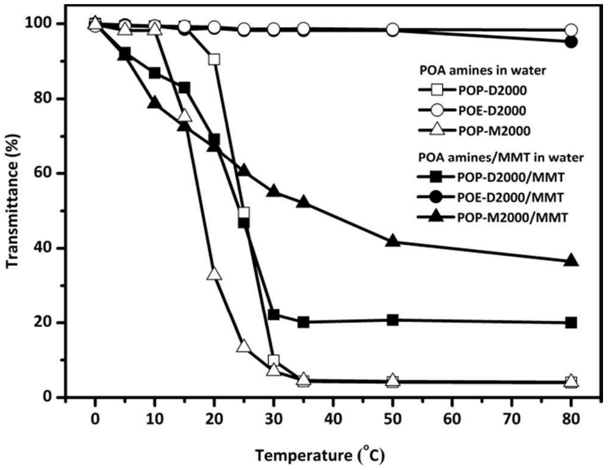


Figure 1. UV-visible transmittance of POP-M2000, POP-D2000, and POE-D2000 solubility in water and their organoclays aggregation over temperature change.

aggregated in water depending on the temperature. Above LCAT, the hydrogen bonding was weakened or disrupted by thermal energy which caused the intercalated POP molecular coils to shrink and phase out from water. As a result, the POP-MMT organoclays aggregated into lumpy precipitates at the elevated temperature. The phenomenon can be measured by using UV-visible transmittance. As shown in Figure 1, the transmittance dropped suddenly due to the occurrence of turbidity upon a critical temperature, which was defined as LCAT. The LCAT of POP-D2000/MMT was in the range of 15–30 °C and LCAT of the analogous POP-M2000/MMT was around 10– 50 °C. It was noted that the POE intercalated MMT had maintained its dispersion state without phase aggregation during heating (Figure 2-e and -f), in contrast to the POP/MMTs (Figure 2-a vs. -b and -c vs. -d). The observed LCAT properties as well as the aggregation phenomena were summarized in Table 2, indicating the lacking of LCAT for the organoclays with a less amount of POP intercalation. All of POP-amines including POP-M300, POP-M1000, POP-M2000 and POP-D2000 intercalated MMT over 1.0 CEC equivalent ratio exhibited the temperature-responsive property. While at low amounts of POP intercalation such as 0.3, 0.5, and 0.7 CEC ratio of POP-M2000 intercalation, 0.3 of POP-D2000 and the pristine Na$^+$-MMT, none of LCAT property was observed. These results showed the POP-modified MMT could be tailored for their hydrophobic interaction.

3.3 Oil-Absorbing Efficiency

The POP tailored organoclays were utilized for oil absorption. As summarized in Table 2, the water-soluble POE-amine derived organoclay had none of oil-absorbing ability due to the lacking of hydrophobic interaction. The oil-absorbing ability was observed for the organoclays intercalated by the POP-amines including POP-M300, -M1000, -M2000, and -D2000 amines. Their maximal capacities were measured by incrementally adding oils and monitoring the oil/clay aggregation or phase separation from water until no further absorption for additional oils. The efficiency of oil absorption

Figure 2. Photo images of the aggregation of organoclays (0.20 g in 10 g water) under temperature change; POP-M2000/MMT (a) 0 °C, (b) 50 °C; POP-D2000/MMT (c) 0 °C, (d) 50 °C ; and POE-D2000/MMT (e) 0 °C, (f) 50 °C.

(η) was calculated based on the equation (1), where $m_{\text{oil absorbed}}$, m_{POP}, and m_{MMT} were the mass by weight of absorbed oil, intercalated POP in clay, and the MMT clay, respectively. The results are summarized in Table 2, for example, the efficiency or the weight ratios was shown to be 10, 12, 15, and 10 folds for the POP-amines, -M300, -M1000, -M2000, and -D2000 intercalated MMT, accordingly.

$$\eta = (m_{\text{oil absorbed}}) / (m_{\text{POP}}) + (m_{\text{MMT}}) \qquad (1)$$

The results are summarized in Table 2, for example, the efficiency or the weight ratios were shown to be 10, 12, 15, and 10 folds for the POP-amines, -M300, -M1000, -M2000, and -D2000 intercalated MMT, accordingly. It is noted the maximal efficiency is reached by the proper amount of POP intercalation into MMT based on the clay CEC capacity.

In order to understand the kinetics of oil absorption, the progressive silicate interlayer spacing were monitored by X-ray diffraction analyses. The organoclays were prepared from POP-M2000 with different basal spacing depending on the amount of POP intercalation based on clay CEC. Several different equivalent CEC including 0.3, 0.5, 0.7, 1.0, 2.0 and 4.0 POP/clay (CEC) ratios were involved as mentioned above. Each of these organoclays was added oils in the amount of 1 to 1 weight ratio. After the absorption, the oil-absorbed organoclays were analysed to be increased basal spacing after absorbing oils within the clay primary layered structure. For example, the basal spacing was expanded from 18 Å to 78 Å (0.3 CEC POP intercalation), 72 Å to 88 Å (0.5 CEC), 71 Å to 84 Å (0.7 CEC), 73 Å to 95 Å (1.0 CEC), 84 Å to 103 Å (2.0 CEC), and 100 Å to 108 Å (4.0 CEC) after oil encapsulation. With further addition of more crude oil beyond 1 to 1 weight ratio, the clay spacing continued to expand. The expansion was reasonable due to the accommodation for more amount of oils. This result was consistent with the previous findings,[17] in which a relatively linear correlation between oil absorption and spacing expansion was observed. Figure 3 showed XRD patterns of POPM2000/MMT at 1.0 CEC clay intercalation, indicating the expansion of clay spacing from 84 Å to featureless by XRD, upon further incremental oil addition. Overall, the oil-absorbing capacity was accompanied by the clay basal spacing expansion and the hydrophobic interaction eventually reaches the maximal when the clay layered structure is exfoliated into XRD featureless measurement. At this point, the added oil is phase separation clearly from water.

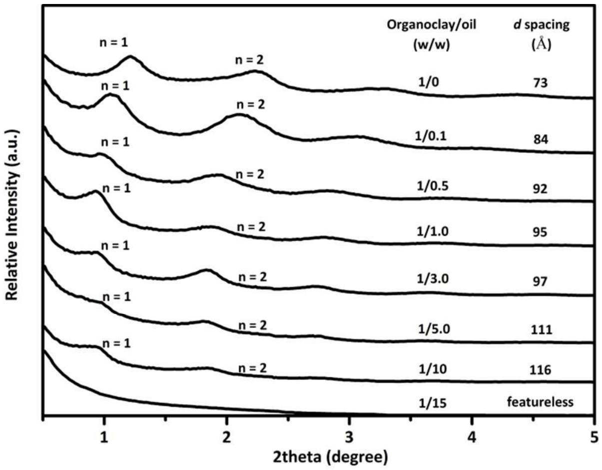
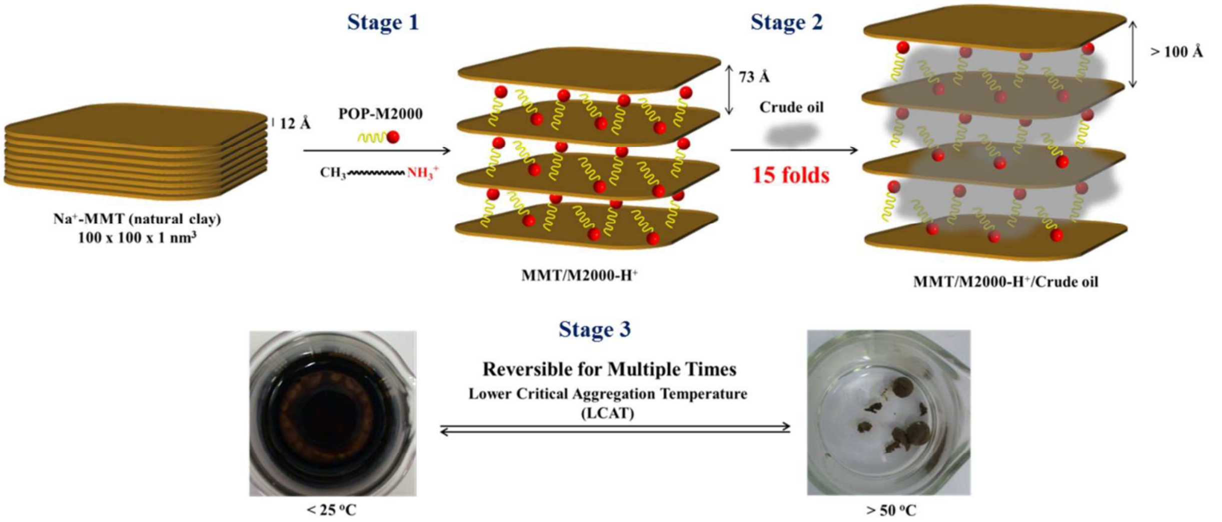


Figure 3. Basal spacing changes after adding incremental amounts of oil absorption in the case of POP-M2000/MMT while adding oil from 0.1 to 15 folds by weight.

In short, the high oil-absorbing efficiency was mainly rendered by the presence of POP organics that was intercalated in the MMT clay. It appeared that the weight fraction of the POP intercalated in the first stage of ionic exchange reaction was responsible for the efficiency of absorbing oils. The further accommodation of incoming oils is dominated by the species of POP-amines which maintain the layered structural container until the exfoliation by the overwhelming oil absorption as the maximal efficiency.

3.4 Oil/Water Separation

The POP-amines in the clay galleries played the most important role for contributing to the efficiency of oil absorption as the oil/water phase separation. The LCST property of the intercalated POP-amines can contribute the behaviour of temperature-depending aggregation and oil separation. The oil contamination in water or the emulsion state of oil/water mixing could be effectively eliminated by adding the POP-MMT organoclay in forming easily separated oil lumps in water. Incorporated with the LCAT property, the overall cleaning process could be designed in three stages: (1) the POP-amines intercalation into MMT to prepare a considerable hydrophobic expansion of the layered silicate structure, (2) the oil absorption by the organoclays undergoing an oil encapsulation and further expanded the clay basal spacing, and (3) the application of LCAT effect on inducing a clear oil-water phase separation by raising the temperature. In general, the selected POP-M2000 organoclay at the temperature above LCAT rendered the absorbed oils aggregated into lumps, spontaneously separated from water. The breaking of water-oil emulsion was conceptually illustrated by the encapsulation of oils in the layered silicate structure and demonstrated by the experiment showing a clear water separation, in Scheme 1. The process of oil absorption in three stages including the preparation of organoclays, oil absorption accompanying with XRD basal spacing changes, and temperature raisings above LCAT for clean phase separation is presented. This three-staged process was examined by the analyses of the changes in organic fraction (by TGA) and primary units of layered silicate interlayer spacing enlargement (by XRD). The TGA technique was able to recognize the absorbed oils from the POP organics dissociation process under the heating pattern (Figure 4). Further, owing to the heat-blocking nature of layered silicates, the delayed degradation phenomenon in TGA may differentiate the oil in the clay interlayer spacing and just surrounding freely on clay surface.[18] The implementation of high efficient oil/water separation was largely relied on the POP hydrophobic and LCST characteristics.



Scheme 1. Proposed oil-absorbing process for the primary unit of POP-layered-silicates and their secondary oil phase segregation from water.

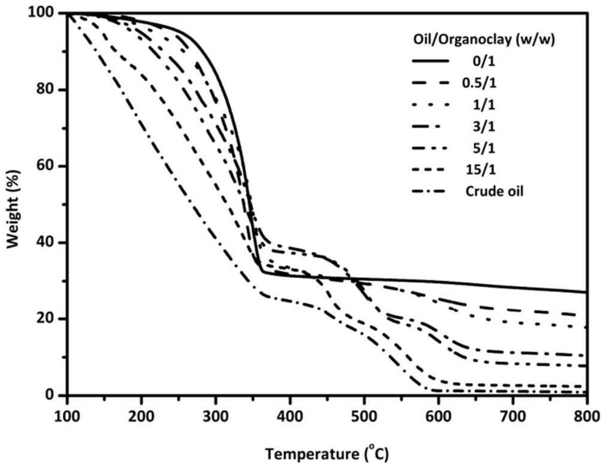


Figure 4. TGA traces of the POP-M2000/MMT at 1.0 CEC intercalation after oil absorption.

The initial oil encapsulation in the layered structure and the second stage of oil absorption in expanding the layered spacing into randomized structure, as well as forming oil lumps by raising temperature above LCAT have completed the process for clear water separation. The overall process was demonstrated in an attached video (see Supporting Information).

4. Conclusion

We used hydrophobic POP-amines to modify the natural silicate clays and successfully demonstrate their effectiveness for the applications of petroleum oil recovery from water. After screening the behavior of five different polyether-backboned amines including water-soluble POE- and hydrophobic POP-amines of different molecular weights, the POP-M2000 monoamine-salt intercalated clays exhibited the highest efficiency of 15 times the weight for oil absorption. Since the pristine clay and the hydrophilic POE-intercalated clays showed none of affinity for oils, the hydrophobicity of the intercalated POP organics is required for oil absorption. The POP-monoamine allowed the single point intercalation in results the spatial expansion of the clay and hydrophobic properties. During the oil incorporation, the spatial galleries were further expanded from 73 Å to >116 Å or featureless XRD. Furthermore, the incorporated POP-amines rendered the clay a LCST property and the influence of oil-absorption through the organoclay aggregation above the critical temperature. As a result, the large oil lumps were separated out from water at ~50 ºC. Hence, the selection of the hydrophobic POP-monoamine favored the oil absorption and phase separation from clean water. The selected POP-intercalated clays are suitable for the applications of oil-spill remediation. The method of organic intercalation could afford a family of organoclay structures which have potential applications in secondary oil recovery, shale-oil fracking and waste water treatment.

Supporting Information

A supporting file of video is supplied for demonstrating the process of crude oil absorption under LCAT phenomenon. This material is available free of charge via the Internet.

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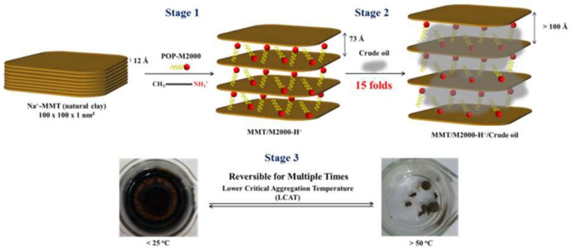
Graphical Abstract/ Table of Content



High efficiency organoclays in absorbing crude oil and clearly separated from water via LCAT.