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Empirical Relationship among the Parameters in HLD Equation of Block Polyether Water Clarifier

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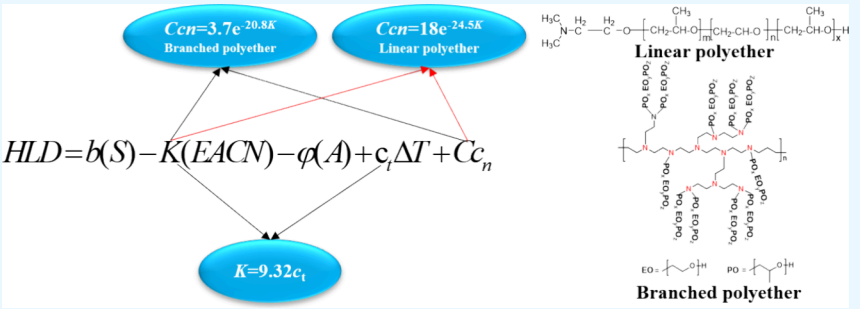

ABSTRACT: In this work, the empirical relationship among three apparent parameters in the hydrophilic−lipophilic deviation (HLD) equation was studied to provide help in using the HLD equation to design a block polyether water clarifier for treating produced water in an oilfield. Ten block polyethers (including six linear polyethers and four branched polyethers) were prepared, and their HLD equations were measured. By curve fitting, the empirical relationship among apparent hydrophobicity characteristic (K), apparent characteristic curvature (Cc_n), and apparent temperature coefficient (c_t) of block polyether were obtained: $K = 9.32c_t$, $Cc_n = 18e^{-24.5K}$ (for linear polyether), and $Cc_n = 3.7e^{-20.8K}$ (for branched polyether). By introducing these relationships into the HLD equation and combining an empirical relationship between propylene oxide/ethylene oxide (mole ratio) in a block polyether and K/Ccn, a new block polyether was designed to treat the produced water. The treatment result confirmed the reliability of these empirical relationships. The results expand the practical application of HLD theory and are useful for the development of a block polyether water clarifier.

1. INTRODUCTION

During the development of an oilfield, a large amount of oily wastewater (usually also known as produced water) is produced.[1,2] Before reuse or discharge of produced water, oil removal treatment is required, and the most commonly used treatment method is to add a water clarifier.[3−5] Usually, two types of organic water clarifiers are used in an oilfield, including a cationic polymer[6−8] and nonionic polyether water clarifier.[9,10]

Cationic polymers can destroy the stability of oil droplets in water through electrostatic neutralization and achieve oil−water separation through flocculation. It has the advantages of low dosage and fast flocculation, but it will produce sticky flocs and oil sludge.[11,12] Nonionic polyether can destroy the collision stability of oil droplets in water by reducing the strength of the water−oil interface and realizes oil−water separation through demulsification. There is no oil sludge produced when nonionic polyether is used.[13,14] Because the oil sludge produced by a nonionic polyether water clarifier is much less than that of a cationic polymer,[15,16] it has been increasingly widely used. Usually, a nonionic polyether water clarifier is prepared by anionic polymerization using ethylene oxide (EO) and propylene oxide (PO) as monomers and a compound containing active hydrogen as an acceptor. The main action mechanism of a nonionic water clarifier is to reduce the strength of the oil−water interface to achieve oil−water separation. Its performance is closely related to the properties of crude oil, salinity of water, and temperature. In our previous works, two series block polyether water clarifiers including linear polyether and branched polyether were prepared,[17,18] and they were suitable for treating different produced waters obtained from different oilfields. When the conditions (crude oil, salinity, and temperature) change, it is also necessary to change the nonionic polyether to fit the new conditions. Therefore, at present, the development of a

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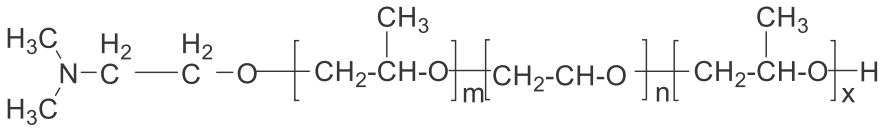
Table 1. EACN of Crude Oil and the Characteristics of Produced Water

	ionic concentration (mg/L)										
water sample	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	CO_3^{2-}	HCO_3^-	SO_4^{2-}	salinity (mg/L)	oil content (mg/L)	EACN
produced water A	3556	230	102	62	5283	0	1298	213	10744	1945	7.7
produced water B	1703	46	181	19	2522	16	491	4	4982	1330	7.9



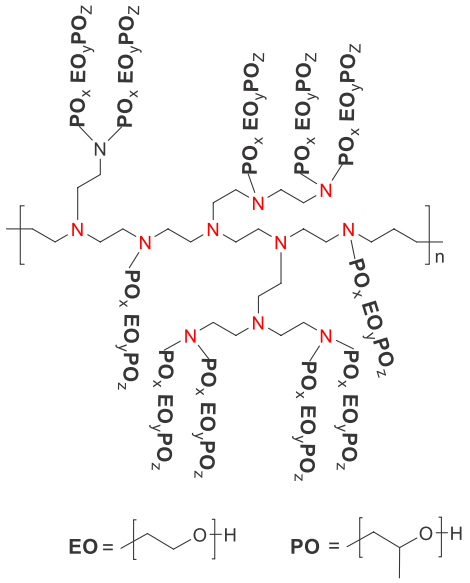


Figure 1. Structural formula of DMEA and PEI series polyethers.

nonionic polyether water clarifier mainly relies on a trial and error method.

Produced water is an oil in water (O/W) type emulsion, and the nonionic polyether water clarifier is a nonionic surfactant. After the addition of a nonionic polyether water clarifier into produced water, the produced water can be regarded as an emulsion containing a nonionic surfactant. Salager built a linear relationship between variables influencing the phase behavior of a surfactant−oil−water system.[19] According to the literature, the hydrophilic−lipophilic deviation (HLD) equation of nonionic surfactant−oil−water is as shown in eq 1[20]

$$\mathrm{HLD} = b(S) - K(\mathrm{EACN}) - \varphi(\mathrm{A}) + c_t\Delta T + \mathrm{Cc_n} \quad (1)$$

where S is the salinity (g/100 mL), b is the salt constant (0.13 for sodium chloride and 0.1 for calcium chloride), K is the characteristic constant of a nonionic surfactant headgroup, $\mathrm{Cc_n}$ is the characteristic curvature of the nonionic surfactant (its value can range from negative for hydrophilic surfactants (normal micelles) to positive for hydrophobic surfactants (reverse micelles),[21] EACN is the equivalent alkane carbon number of oil, $\varphi(\mathrm{A})$ is a function of alcohol type and concentration, c_t is the temperature coefficient of the nonionic surfactant, and ΔT is the difference between the formulation temperature and the reference temperature (25 °C; in °C). The emulsion stability is related to the HLD of a surfactant−oil−water system; when HLD = 0, the thermodynamic stability of emulsion is the worst.[22−24]

It should be noted that the insights delivered by the HLD theory have been applicable to the demulsification.[14,25] However, there are too many parameters in the HLD equation,[26] such as K, EACN, $\varphi(\mathrm{A})$, c_t, $\mathrm{Cc_n}$, and so it is not easy to use the HLD equation to guide the quantitative design of a nonionic block polyether water clarifier. After careful analysis of the HLD equation, we can find that there are two types of parameters: one type consists of environmental parameters, including S, EACN, $\varphi(\mathrm{A})$, and ΔT; the other type consists of structural parameters of the surfactant, including K, c_t, and $\mathrm{Cc_n}$. If we can find the empirical relationship among K, c_t, and $\mathrm{Cc_n}$, the HLD equation can be simplified, and this can be more conducive to guide the preparation of a block polyether water clarifier. In this work, first, ten block polyethers were prepared and their HLD equations were measured and verified by treatment of produced water A. Then, the empirical relationship between K and c_t and the empirical relationship between K and $\mathrm{Cc_n}$ were fitted, and a simplified HLD equation was established. Finally, by combining the simplified HLD equation and the empirical relationship between PO/EO (mole ratio) in the block polyether and $K/\mathrm{Cc_n}$, a block

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polyether water clarifier was designed to treat the produced water B. The treatment result confirmed the reliability of the simplified equation. This paper represents a positive attempt to use the HLD equation to guide the design of PO/EO in a block polyether water clarifier, expanding the practical application of HLD theory, and the results are useful for the development of block polyether water clarifiers.

2. MATERIALS AND METHODS

2.1. Materials. Hexane (C6, EACN = 6), heptane (C7, EACN = 7), *n*-octane (C8, EACN = 8), *n*-decane (C10, EACN = 10), *N*,*N*-dimethylethanolamine (DMEA), polyethylenimine (PEI), EO, PO, and NaCl were analytically pure and were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. The produced water A and produced water B were obtained from the Bohai offshore oilfield. The crude oil A density was 0.9364 g/cm^3, and the SARA contents were 40.08 wt % saturates, 36.50 wt % aromatics, 17.00 wt % resins, and 8.35 wt % asphaltenes. The crude oil B density was 0.9417 g/cm^3, and the SARA contents were 32.77 wt % saturates, 38.74 wt % aromatics, 17.22 wt % resins, and 11.27 wt % asphaltenes. Their EACNs were measured according to our previous work,[27] and they are shown in Table 1. In addition, the characteristics of produced water are listed in Table 1.

2.2. Preparation and Characterization of Block Polyether Water Clarifier. *2.2.1. Preparation.* DMEA and PEI were used as acceptors, and two series block polyether water clarifiers were prepared according to refs 17 and 18. Ten block polyethers were obtained in this work. Their typical structures are shown in Figure 1, and structural information is listed in Table 2.

Table 2. Structural Information of Ten Block Polyethers

no.	acceptor	block sequence	block mass ratio	EO/PO	abbreviation
1	DMEA	EP	3:5	3:5	D1
2		PE	5:3	3:5	D2
		EPE	0.3:5:2.7	3:5	D3
3		PEP	1:6:9	3:5	D4
5		PEP	1:8:9	4:5	D5
6		PEP	1:10:9	5:5	D6
7	PEI3000	EPE	0.3:5:2.7	3:5	P1
8		PEP	1:6:9	3:5	P2
9		PEP	1:8:9	4:5	P3
10		PEP	1:10:9	5:5	P4

Taking the preparation of D4 as an example, the specific synthesis steps are described as below. A high-pressure stainless steel autoclave (2 L capacity) was utilized to achieve both propoxylation and ethoxylation reactions. First, the propoxylation of DMEA was carried out according to the following process: DMEA (10 g) and KOH (3.0 g, acting as a catalyst) were added into the autoclave. The autoclave was vacuumized. Then, the temperature was gradually raised to 135 °C. Finally, 990 g of PO was introduced gradually (with the pressure in the autoclave kept lower than 0.4 MPa) through a pressure pipet mounted over the inlet valve, which was connected to a nitrogen cylinder. Nitrogen was utilized to force the PO inside the reactor. And the stirrer was set at a speed of 300 rpm. As PO was consumed in the reaction, the pressure dropped to a minimum, and all the PO was consumed. Heating was stopped, and the contents were cooled gradually to ambient temperature with cold water by means of a cooling coil inside the reactor. Then the intermediate compound propoxylated DMEA was obtained to conduct the next ethoxylation.

Propoxylated DMEA (100 g) and KOH (0.9 g) were placed in the autoclave at first. Then, 600 g of EO was introduced to do the ethoxylation. The reaction conditions for ethoxylation are similar to those of the propoxylation with the exception of the temperature set to be 120 °C instead of 135 °C. After this ethoxylation, according to a similar method, 1000g of PO was put in the autoclave successively and consumed. At last, D4 was obtained.

2.2.2. Characterization. The FT-IR spectra were collected on a WQF520 infrared spectrometer (Rui li Analytical Instrument Co. Ltd., China) with a wavelength range of 4000−500 cm^{-1} and a resolution of 4 cm^{-1}. The ^{1}H NMR spectra were obtained using an AVANCE NEO600 NMR spectrometer (Bruker, Germany) with $CDCl_3$ as the solvent. The number average molecular weight (M_n), weight average molecular weight (M_w), and molecular weight distribution index (MWD) were determined by a PLGPC 50 gel permeation chromatograph (Agilent, USA).

2.3. HLD Equation Measurement of Block Polyether. The HLD equation of block polyether was measured according to ref 27. Block polyether is a nonionic surfactant. The expression of its HLD equation is shown in eq 1. Since there was no alcohol present in the produced water and the EACN of crude oil was known, the HLD equation could be determined as long as K, Cc_n, and c_t were determined.

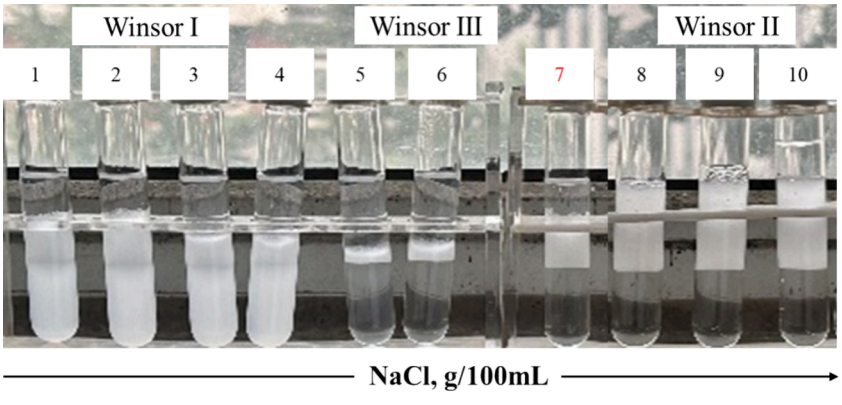

Figure 2. Salinity scan samples for S^* measurement.

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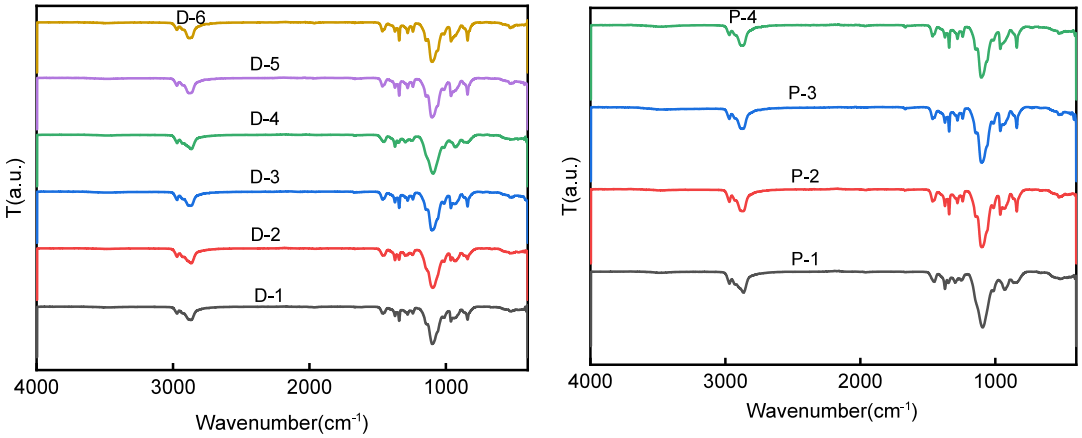

Figure 3. IR spectra of block polyethers.

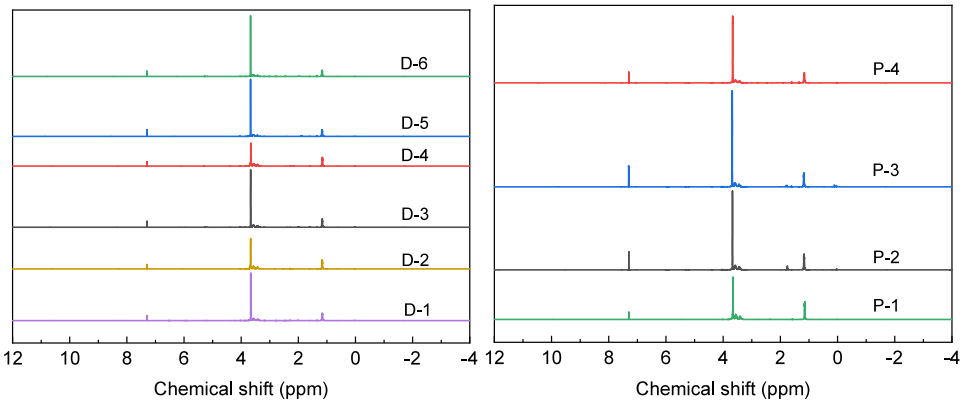

Figure 4. ^{1}H NMR spectra of block polyethers.

For the alcohol-free system, $\varphi(\mathrm{A}) = 0$. The HLD equation of the nonionic surfactant can be rewritten as eqs 2 and 3.

$$b(S^*) = K(\mathrm{EACN}) - c_t(T - 25) - \mathrm{Cc_n} \quad (2)$$

$$b(S^*) = -c_t(T - 25) + K(\mathrm{EACN}) - \mathrm{Cc_n} \quad (3)$$

To obtain K, $\mathrm{Cc_n}$, and c_t, the specific experimental steps are as follows. First, 1 wt % block polyether aqueous solution was used as the water phase to screen the optimal salinities (S^*) of oil phases having different EACNs at 25 °C. The relationship of $b(S^*)$ vs EACN was fitted according to eq 2. K and $\mathrm{Cc_n}$ were calculated according to the slope and intercept of eq 2. Then, the EACN of the oil phase was fixed as 8.0 to screen the optimal salinities at different temperatures, and the relationship of $b(S^*)$ vs $(T - 25)$ was fitted according to eq 3. c_t was calculated according to the slope of eq 3. The HLD equation of block polyether was obtained by substituting K, $\mathrm{Cc_n}$ and c_t into eq 1.

The method of obtaining S^* is as follows. First, 5 mL of oil phase and 5 mL of NaCl aqueous solution containing block polyether (1 wt %) were put into the test tube; then, the tube was shaken by hand 20 times and allowed to stand for 1 day to observe the layering phenomenon. If the emulsion is Winsor III type (see Figure 2), the salinity is the optimal salinity S^* and HLD = 0 at this time.

It should be noted that as the emulsion is not really a microemulsion, referring to the concept of apparent equivalent alkane carbon number used in ref 28, the parameters K, $\mathrm{Cc_n}$, and c_t in this paper can be considered as the apparent parameters.

2.4. Oil−Water Interfacial Tension (IFT) Measurement. The IFT was measured by using a TX-500C rotating drop interfacial tensiometer (CNG, USA) at a spinning speed of 5000 rpm, and the equilibrium IFT was recorded. The oil phase was *n*-octane, and the aqueous phase was 50 mg/L block polyether.

2.5. Test of Produced Water Treatment. The bottle test was conducted according to ref 27. First, 20 mL of produced water was added into the test bottle, and it was preheated in a water bath at the set temperature for 10 min. Then, block polyether aqueous solution was added into the bottle, the bottle was shaken by hand 40 times, and the mixture was left to stand in the water bath for 20 min. Finally, 10 mL of water was taken from the bottom of the test bottle into a cylinder, and 5 mL of *n*-hexane was added to extract the crude oil in the water. The *n*-hexane solution was taken into the test tube of oil content analyzer TD-500 (Turner, USA) to measure the oil content, and the oil removal was calculated (see eq 4)

$$\text{oil removal} = (C_0 - C_a)/C_0 \times 100\% \quad (4)$$

where C_0 is the initial oil content of produced water and C_a is the oil content of produced water after treatment. Each experiment was repeated twice.

3. RESULTS AND DISCUSSION

3.1. Characterization Results of Block Polyether. Figure 3 shows the IR spectra of block polyethers. The

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Table 3. Molecular Weights of Block Polyethers

no.	block polyether	n(EO):n(PO)[a]	n(EO):n(PO)[b]	M_n (g/mol)	M_w (g/mol)	MWD
1	D1	0.79:1	0.78:1	2271	4405	1.94
2	D2	0.79:1	0.79:1	2661	4518	1.70
3	D3	0.79:1	0.80:1	2455	4694	1.91
4	D4	0.79:1	0.79:1	2468	4996	2.02
5	D5	1.05:1	1.04:1	2859	4808	1.68
6	D6	1.32:1	1.33:1	2638	4985	1.89
7	P1	0.79:1	0.80:1	2454	3466	1.41
8	P2	0.79:1	0.79:1	3235	5072	1.57
9	P3	1.05:1	1.04:1	2949	4343	1.47
10	P4	1.32:1	1.33:1	2697	4017	1.49

[a]Experimental feeding ratio. [b]Measurement value by ^{1}H NMR.

bands at 2970 and 1110 cm^{-1} are ascribed to the stretching vibration absorptions of $-CH_3$ and C−O−C, respectively, which are the characteristic absorption peaks of block polyether. Figure 4 shows the ^{1}H NMR spectra of block polyethers. The characteristic methyl group signal of the PO block appears at 1.14 ppm, and the methylene and methine group signal of the EO and PO block appears at 3.54 ppm. The molar ratio of EO to PO in the polyether can be calculated according to the their peak areas in the ^{1}H NMR spectra (see eq 5).[17]

$$n(\mathrm{EO}):n(\mathrm{PO}) = [(S_{3.54} - S_{1.14})/4]/(S_{1.14}/3) \quad (5)$$

After the calculation, it was found that the polyether had a predicted molar ratio of EO to PO (see Table 3). In addition, Table 3 lists the molecular weights of block polyethers. We can find that they had similar M_ns, which were in the range of 2200−3200 g/mol.

Table 4. HLD Equations of Block Polyethers

no.	block polyether	HLD equation
1	D1	HLD = 0.13S − 0.181EACN + 0.019ΔT + 0.436
2	D2	HLD = 0.13S − 0.168EACN + 0.017ΔT − 0.141
3	D3	HLD = 0.13S − 0.189EACN + 0.018ΔT − 0.539
4	D4	HLD = 0.13S − 0.154EACN + 0.015ΔT + 0.428
5	D5	HLD = 0.13S − 0.161EACN + 0.017ΔT + 0.334
6	D6	HLD = 0.13S − 0.187EACN + 0.019ΔT + 0.186
7	P1	HLD = 0.13S − 0.130EACN + 0.012ΔT − 0.618
8	P2	HLD = 0.13S − 0.134EACN + 0.013ΔT + 0.245
9	P3	HLD = 0.13S − 0.160EACN + 0.017ΔT + 0.122
10	P4	HLD = 0.13S − 0.227EACN + 0.022ΔT + 0.034

3.2. HLD Equation of Block Polyether. The measurement results of $b(S^*)$ vs EACN and $b(S^*)$ vs ΔT are shown in Figure 5. Based on the fitting result shown in Figure 5a,c, the apparent K and apparent Cc_n were obtained, while based on the fitting result shown in Figure 5b,d, c_t was obtained. According to the results of the apparent K, the apparent Cc_n and apparent c_t were obtained. The HLD equations of block polyethers were obtained, and they are listed Table 4. Based on the results in Table 3, we can find that the HLD equation was affected by the PO/EO ratio, block sequence, and molecular configuration. There are three insights for us. (1) When the EO segment was at the end of the polyether chain, the apparent Cc_n is negative, which indicated that it was conducive to the formation of an O/W emulsion. (2) The apparent c_t increased with the increasing EO content (see Figure 6a),[29] indicating the temperature sensitivity of polyether increased

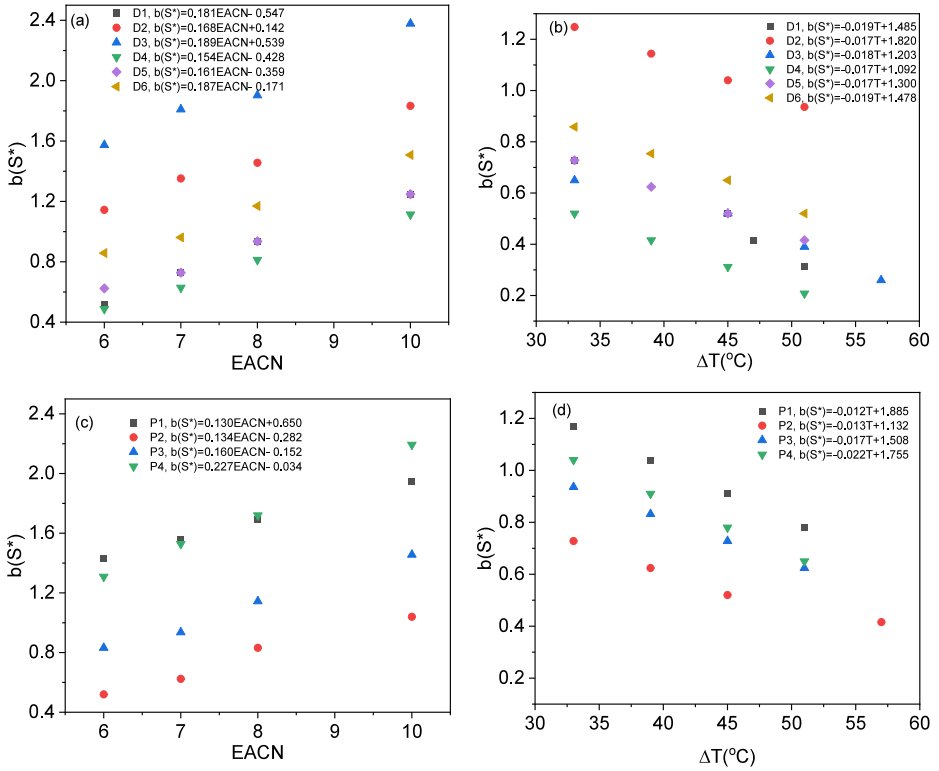

Figure 5. (a) $b(S^*)$ vs EACN at 25 °C of the D series. (b) $b(S^*)$ vs ΔT at EACN = 8 of the P series. (c) $b(S^*)$ vs EACN at 25 °C of the P series. (d) $b(S^*)$ vs EACN at 25 °C of the P series.

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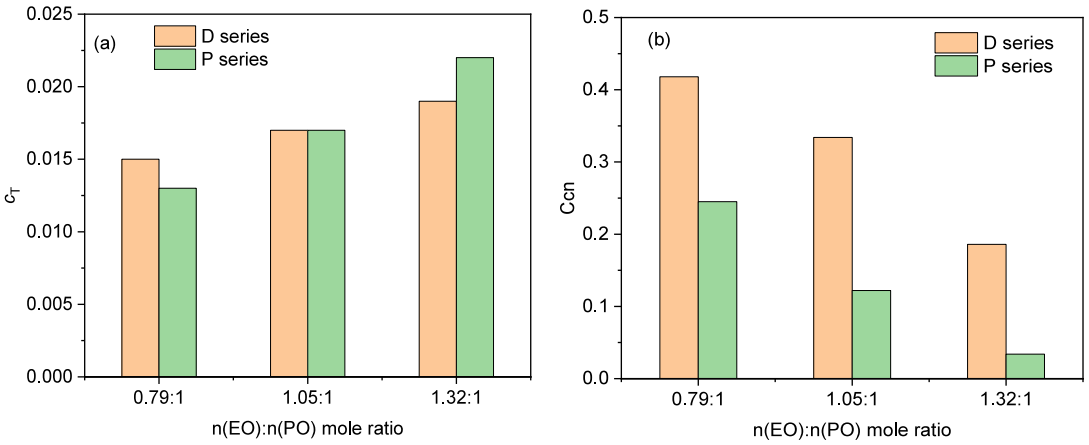

Figure 6. Effect of EO/PO mole ratio on c_t (a) and Cc_n (b).

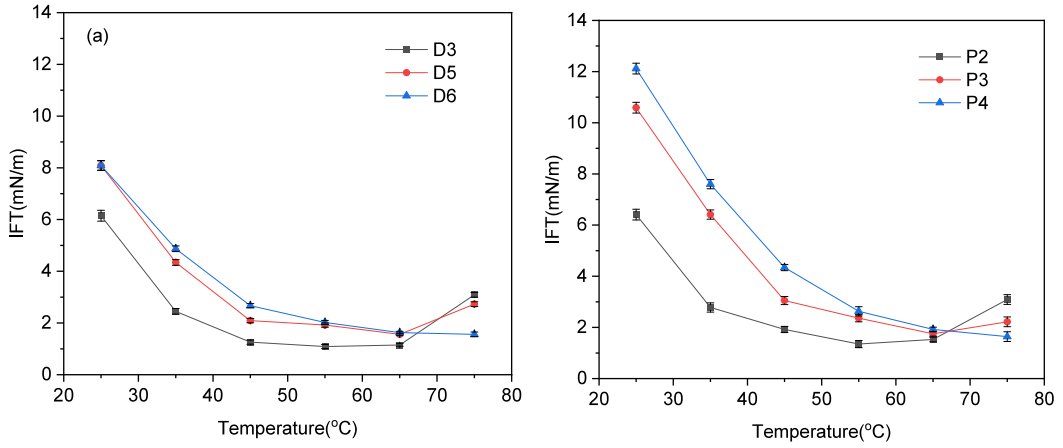

Figure 7. Relationship between IFT and temperature of different polyethers: (a) D series; (b) P series. The oil phase was *n*-octane, and the aqueous phase was 50 mg/L block polyether.

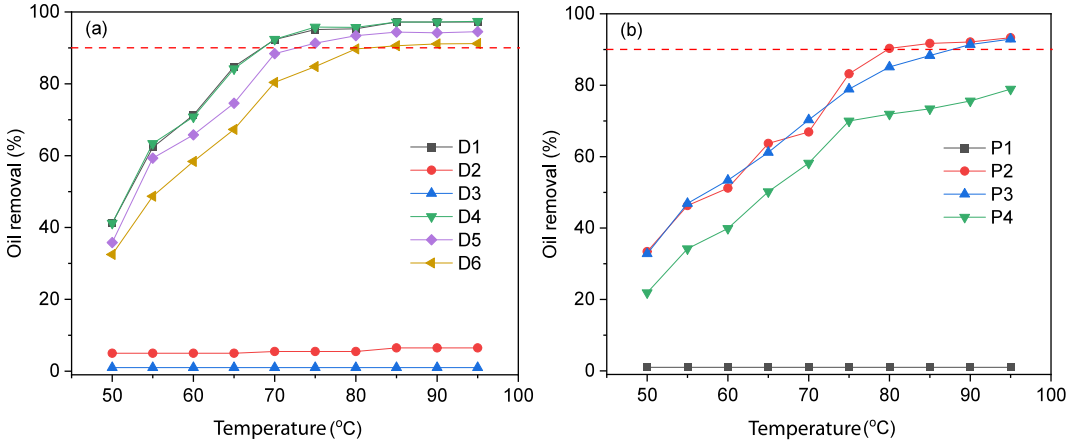

Figure 8. Oil removals of different block polyethers for treating produced water A at different temperatures: (a) DMEA series polyether; (b) PEI series polyether. The polyether concentration was 200 mg/L.

with the increasing EO content. A greater temperature sensitivity means a higher phase inversion temperature of the polyether. In this work, the phase inversion temperature of the polyether was obtained by IFT measurement at different temperatures (see Figure 7). Usually, the IFT has the lowest value at the phase inversion temperature.[30] It was found that the phase inversion temperature of both D series and P series polyethers increased with the increasing EO content, which confirmed that the apparent c_t increased with the increasing EO content. (3) As the EO content increased, athe pparent Cc_n gradually decreased (see Figure 6b), indicating that the polyether tends to form normal micelles in water, and HLD had more difficulty in approaching 0.

In addition, in order to verify the correctness of these HLD equations, produced water A treatment experiments were carried out. Produced water A was used to investigated the

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Table 5. Temperature Comparison between HLD Equation Predicted and Experiment Measured

no.	block polyether	temperature predicted by T(HLD = 0) (°C)	temperature measured by experiment (°C)	relative error (%)
1	D1	68.6	68.7	0.14
2	D2	101.0	>95	
3	D3	66.8	68.7	2.84
4	D4	128.0	>95	
5	D5	70.6	72.8	3.12
6	D6	84.2	82.5	−2.02
7	P1	149.1	>95	
8	P2	75.5	80.0	5.96
9	P3	82.6	88.0	6.54
10	P4	97.0	>95	

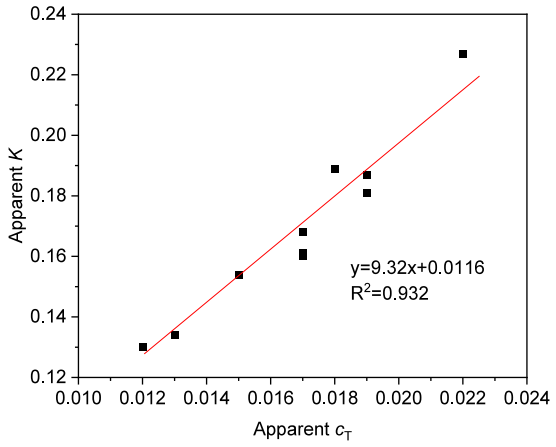

Figure 9. Fitting relationship between K and c_t.

performance of the block polyethers at different temperatures, and the results are shown in Figure 8. As shown in Figure 6, with an increase in temperature, the oil removals of some block polyethers showed a gradually increasing trend and the others (including D2, D3, and P1) had no change. From the perspective of structure, D2, D3, and P1 have an EO segment at the end of the polyether chain. According to ref 31, when the EO segment was at end of the polyether chain, the polyether was suitable for the demulsification of a water-in-crude oil (W/O) emulsion, while the produced water is a O/W emulsion. Therefore, the oil removal of D2, D3, and P1 was small. From the perspective of HLD theory, this is because as the temperature increased, the HLD of polyether gradually approached zero, the oil droplet stability in produced water gradually decreased, the oil removal gradually increased, and the produced water gradually became clear. The HLDs of D2, D4, and P1 were far from zero; therefore, their oil removals were very small and did not increase when the temperature increased. Similar to our previous work,[27] in order to quantitatively analyze the effect of the molecular structure on the treatment performance of the block polyether, the temperature corresponding to oil removal of 90% was defined as the onset temperature of the polyether as well as the temperature corresponding to HLD = 0. Table 5 lists the onset temperatures predicted by HLD theory and experimental measurement. It can be seen that the temperature predicted by HLD theory had a small error compared with that of the experimental measured temperature. This experimental result indicated that the HLD equations listed in Table 4 were right.

3.3. Relationship between Various Parameters in HLD Equation. By fitting the relationship between the apparent K and apparent c_t, we can find that they have a good linear relationship (see Figure 9), $K = 9.32c_t$, which is suitable for the D series and P series polyethers.

By fitting the relationship between apparent K and apparent Cc_n, we can find that there was an exponential relationship between the apparent K and apparent Cc_n (as shown in Table 6 and Figure 10). However, D series and P series polyethers had different fitting results. The result may be mainly related to their characteristics of micelle formation. K is the characteristic constant of the nonionic surfactant headgroup, which is usually determined by PO/EO ratio, while Cc_n is the characteristic curvature of nonionic surfactant micelles, which has a great relationship with the polyether molecular configuration. In this work, D series are linear polyethers and P series are branched polyethers, and they had different molecular configurations. Therefore, when they had similar apparent K values, the apparent Cc_n values were very different. According to ref 32, we can find that the aggregation behavior of a branched polyether is different from that of a linear polyether. The aggregation number of a branched polyether for formation of spherical micelles is smaller than that of a linear polyether, and a branched polyether is more likely to form wormlike micelles. This may be the reason the branched polyether had a lower Cc_n.

Introducing the relationship between the apparent K and apparent c_t and the relationship between the apparent K and apparent Cc_n into the HLD equation, we can obtain a simplified HLD equation. For the D series polyethers, the simplified HLD equation is as follows:

$$\mathrm{HLD} = b(S) - K(\mathrm{EACN}) + \frac{K}{9.3}\Delta T + 18e^{-24.5K} \quad (6)$$

For the P series polyethers, the simplified HLD equation is as follows:

$$\mathrm{HLD} = b(S) - K(\mathrm{EACN}) + \frac{K}{9.3}\Delta T + 3.7e^{-20.8K} \quad (7)$$

3.4. Application of Simplified HLD Equation. Produced water B, which was obtained from another offshore oilfield, was used as the treatment object, and the simplified HLD eq 6 was used to design the suitable block polyether water clarifier. For produced water B, the salinity was 5000 mg/L (S = 0.5), EACN was 7.9, and the treatment temperature in the offshore

Table 6. Fitting Results between Apparent K and Apparent Cc_n

D series	block mass ratio	K	Cc_n	P series	block mass ratio	K	Cc_n
PEP	1:6:9	0.154	0.428	PEP	1:6:9	0.134	0.245
PEP	1:8:9	0.161	0.334	PEP	1:8:9	0.160	0.122
PEP	1:10:9	0.187	0.186	PEP	1:10:9	0.227	0.034
fitting result		$Cc_n = 18e^{-24.5K}$		fitting result		$Cc_n = 3.7e^{-20.8K}$	

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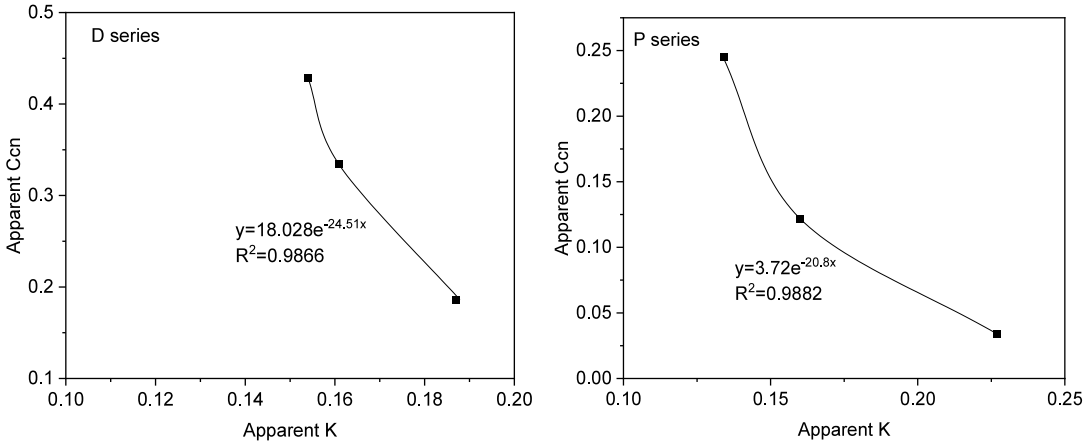

Figure 10. Fitting relationship between apparent K and apparent Cc_n.

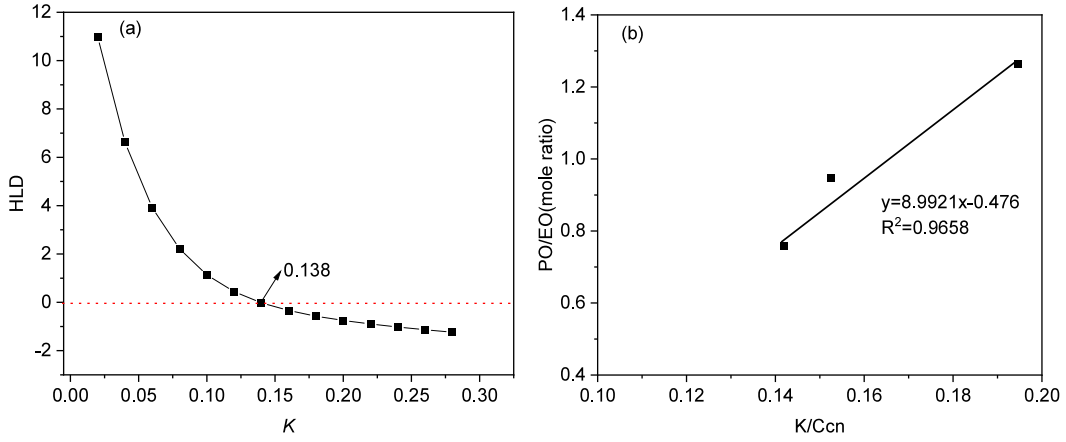

Figure 11. (a) Relationship between K and HLD under another produced water treatment condition, (b) Relationship between K/Cc_n and PO:EO (mole ratio).

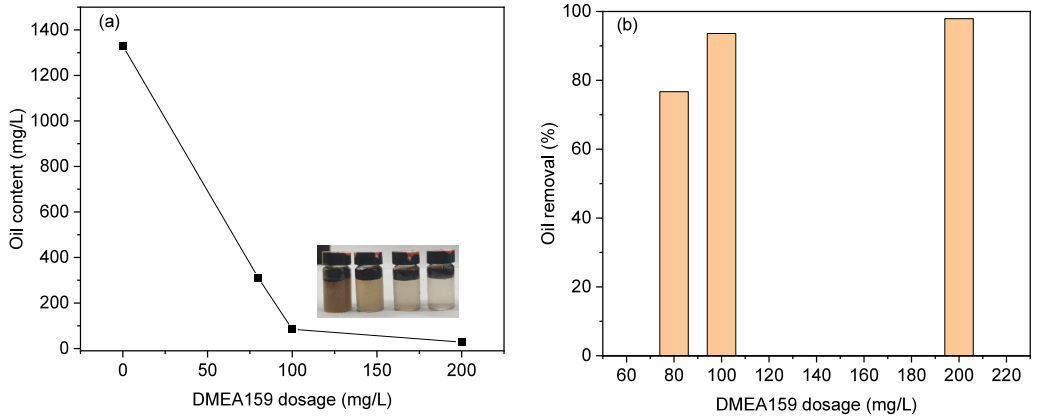

Figure 12. Produced water B treatment by DMEA159 at 55 °C: (a) oil content after treatment; (b) oil removal after treatment.

platform was 55 °C. According to these conditions, the relationship between K and HLD was plotted in Figure 11a. For block polyether water clarifier design, the relationship between K/Cc_n and PO:EO (mole ratio) was found and fitted (see Figure 11b) by using the data presented in Table 6. From Figure 11a, it was found that K was 0.138 when HLD was 0. Substituting K = 0.138 (K/Cc_n = 0.225) into the relationship between K/Cc_n and PO:EO (mole ratio), we can find that the PO:EO (mole ratio) was 1.55:1 (in other words, the PO:EO mass ratio was 2:1). According to this result, a new block polyether water clarifier having a PEP block sequence (1:5:9) was prepared by using DMEA as an acceptor, namely DMEA159. When the temperature was 55 °C, the performance of DMEA159 was evaluated and the results are shown in Figure 12. We found that DMAE159 had good oil removal performance at 55 °C when its dosage was more than 80 mg/L. This result indicated that the simplified HLD equation is useful and effective for the block polyether water clarifier design.

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4. CONCLUSION

The HLD equations of ten block polyethers were measured in this work. It was found that the HLD equation was affected by three factors including the PO:EO ratio, block sequence, and molecular configuration. The apparent Cc_n is negative when the EO segment is at the end of the polyether chain, it decreased with increasing EO content, and the linear polyether had a larger apparent Cc_n than that of branched polyether. The apparent K and apparent c_t increased with the EO content. The empirical relationships among apparent K, apparent Cc_n, and apparent c_t were obtained: $K = 9.32c_t$, $Cc_n = 18e^{-24.5K}$ (for linear polyether), and $Cc_n = 3.7e^{-20.8K}$ (for branched polyether). A simplified HLD equation was established by introducing these relationships into the HLD equation. In addition, PO:EO (mole ratio) in the linear block polyether and K/Cc_n presented a empirical relationship of PO:EO (mole ratio) = 8.992 K/Cc_n − 0.476. Combining the simplified HLD equation and empirical relationship between PO:EO (mole ratio) in the linear block polyether and K/Cc_n, the PO:EO ratio in the block polyether water clarifier can be accurately designed, and DMEA159 was successfully designed for treating the produced water. While the results in this paper were suitable for block polyethers prepared by using DMEA and PEI as acceptors, more samples should be studied in the future.

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Notes

The authors declare no competing financial interest.

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