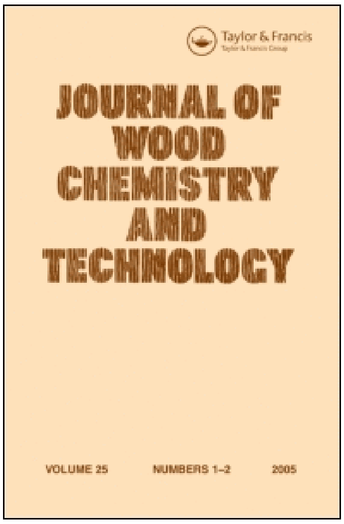

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

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To cite this Article Homma, Harumi , Kubo, Satoshi , Yamada, Tatsuhiko , Matsushita, Yasuyuki and Uraki, Yasumitsu(2008) 'Preparation and Characterization of Amphiphilic Lignin Derivatives as Surfactants', Journal of Wood Chemistry and Technology, 28: 4, 270 — 282

To link to this Article: DOI: 10.1080/02773810802510688

URL: http://dx.doi.org/10.1080/02773810802510688

Journal of Wood Chemistry and Technology, 28: 270–282, 2008

ISSN: 0277-3813 print / 1532-2319 online
DOI: 10.1080/02773810802510688

Preparation and Characterization of Amphiphilic Lignin Derivatives as Surfactants

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Abstract: Acetic acid lignin (AL), one of the organosolv lignins, was modified by polyoxyethylation using commercially available polyethylene glycol diglycidylethers (PEGDE) having various chain lengths in order to generate novel nonionic polymeric surfactants. AL could be converted to the amphiphile by modifying with PEGDE (PEGDE-AL) having more than 9 of the ethylene oxide (EO) repeating units. Although the surface activities of PEG and AL were very limited, PEGDE-AL did strongly depress surface tension of water, and showed clear critical micelle concentrations (CMC). The CMC value of PEGDE-AL could be comparable to a commercial anionic lignin surfactant, lignosulfonate. The surface activity of AL amphiphile was further improved by modification with monoepoxides, ethoxy-(2-hydroxy)-propoxy-polyethylene glycol glycidylether (EPEGGE). The surface tension of water was depressed by the addition of the EPEGGE-AL to the same level as Triton® X-100, which is a commercial PEG-based nonionic surfactant, although there is still room for improvement in CMC value. The hydrophile–lipophile balance (HLB) of these AL amphiphiles was in the range of 11–14, and significant biodegradation was observed. These results suggest that the AL amphiphiles can be used as emulsifier and detergent.

Keywords: Acetic acid lignin, biodegradability, hydrophile–lipophile balance (HLB), surface activity, surfactant

INTRODUCTION

The development of advanced materials derived from woody biomass is drawing increased attention due to environmental concerns associated with the

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This work was supported by a grant from the Ministry of Agriculture, Forestry and Fisheries of Japan (Rural Biomass Research Project, BM-D1321).

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utilization of fossil resources. Lignin, one of the main components of woody biomass, is typically used as a fuel to recover energy in the conventional pulping process, but has also been reported to have potential as a raw material for production of chemicals and materials.[1] As the estimated fuel value of lignin is limited ($0.04 per pound based on the calorific value of coal in the United States[2]), lignin may be more effectively utilized as a raw material for value-added products to make the biomass industry economically feasible and to replace materials derived from fossil sources.

In this perspective, an organosolv pulping process using aqueous acetic acid has been examined to efficiently separate acetic acid lignin (AL) as well as carbohydrate components from lignocelluloses.[3] Due to the thermoplastic nature of AL, it can be utilized as a raw material for molded carbonaceous materials and hot-melt adhesives for fiber board production.[4,5] Moreover, it was found in another application that AL could be converted to an amphiphlic polymer through derivatization with polyethylene glycol diglycidylethers (PEGDE).[6] This AL amphiphile (PEGDE-AL) forms physical and/or chemical complex with cellulase, which prolongs enzyme activity of cellulase for a long period. This result indicates that PEGDE-AL could be a promising support for cellulase in a water-soluble immobilized enzyme system. This favorable property of PEGDE-AL as cellulase stabilizer is assumed to be caused by the weak surface activity of the PEGDE-AL, which facilitates the release of moderate amounts of enzyme from the complex.[7]

Surfactants are widely used in various industries as detergents, emulsifiers, dispersants, stabilizers, and so on. Based on the chemical structure, surfactants are classified into four types: anionic, cationic, zwitterionic, and nonionic surfacants. The PEGDE-AL is potentially utilized as a nonionic surfactant based on its chemical structure. Nonionic surfactants have some advantages compared to the other types. For example, most nonionic surfactants are hypoallergenic to skin surfaces, and can be used in many hard waters as well. Approximately half of the total production of surfactants is nonionic surfactant in Japan, and the production has been increasing yearly. However, surface activity of PEGDE-AL is weak and not enough for surfactant application. Therefore, improvement in surface activity is necessary to utilize PEGDE-AL as a nonionic surfactant.

In this article, PEGDE-AL was modified with PEGDE and its methylated derivatives, having various chain lengths to enhance surface activity. Surface activity was measured as the depression of surface tension of water, and the effect of chemical structures of PEGDE on the surface activity of PEGDE-AL is discussed.

EXPERIMENTAL

Materials

AL was prepared from the spent liquor of the atmospheric acetic acid pulping of birch wood as water insoluble fractions.[3] PEGDEs having different degrees

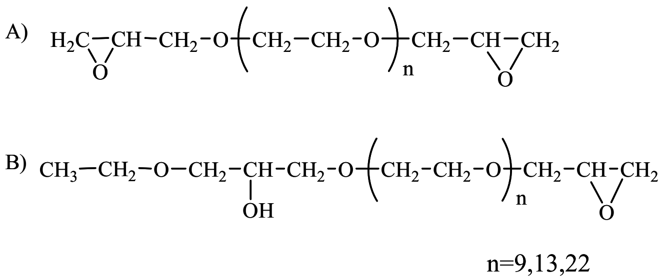

Figure 1. Chemical structure of polyethylene glycol diglycidylether (PEGDE, A) and ethoxy (2-hydroxy)propxy polyethylene glycol glycidylether (EPEGGE, B).

of polymerization (DP) of PEG moiety were obtained from Nagase Chemtex Corp. (Osaka, Japan). Chemical structures of PEGDEs are depicted in Figure 1. Other chemicals in research grade were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). All chemicals were used as received.

Mono-epoxide polyethylene glycol [ethoxy-(2-hydroxy)-propoxy-polyethylene glycol glycidylether, EPEGGE] was prepared from PEGDE by blocking an epoxide group at one end. Three mL of sodium methoxide ethanol solution (1.7 mol/L) was drop-wisely added to equimolar amounts of PEGDE in acetone over 20 min, and then the mixture was stirred for 10 min at 70°C. Reaction products, EPEGGE, were collected as a hexane insoluble fraction and dried *in vacuo*. The supposed mono-substitution reaction was confirmed by signal area ratio of epoxide and substituted methoxy protons in ^{1}H-NMR analysis.

PEGDE. ^{1}H NMR ($CDCl_3$) δ: 2.60 (dd, 1H, CH_2, epoxy, $J = 2.7, 5.0$ Hz), 2.79 (t, 1H, CH, epoxy, $J = 4.2$), 3.16 (m, 1H, CH, epoxy).

EPEGGE. ^{1}H NMR ($CDCl_3$)δ : 1.20 (t, 3H, CH_3, $J = 7.0$), 2.60 (dd, 1H, CH_2, epoxy, $J = 2.7, 5.0$ Hz), 2.79 (t, 1H, CH, epoxy, $J = 4.6$), 3.16 (m, 1H, CH, epoxy), 3.95 (m, 1H, C*H*-OH)

Preparation of Lignin Amphiphiles

AL and an appropriate amount of PEGDE or EPEGGE were dissolved in 1 M NaOH and stirred for 2 h at 70°C. The reaction mixture was acidified with acetic acid to pH 4, and the remaining epoxide compounds and low molecular weight fractions were removed by ultrafiltration (cutoff = 1000 Da). PEGDE-AL (or EPEGGE-AL) was recovered by lyophilization, and dried in a vacuum oven before use.

Weight ratios of PEG component in PEGDE-AL and EPEGGE-AL were determined by the modified Morgan method.[8,9] Using this method, the ether bond in the PEG chain was cleaved with hydroiodic acid, and the consumption of HI was determined as the amount of iodine produced by titration with sodium thiosulfate. Efficiency of this ether cleavage reaction was assessed by titer of sodium thiosulfate in the same decomposition process for standard PEG600. PEG content in PEGDE-AL and EPEGGE-AL estimated from titer of sodium thiosulfate was corrected for the reaction efficiency value.

Measurement of Surface Tension

Surface tension measurements were carried out by the ring method using a Du Nouy tensiometer.[10] Pure water (electrical resistivity $= 18.2\ \mathrm{M\Omega \cdot cm^{-1}}$) was used in this measurement. Measurements were done after 6–10 min following the sample addition and surface tension values were shown in the average values of three different measurements. Critical micelle concentration (CMC) values were identified as the discontinuity point on the surface tension versus logarithm of concentration plot. Time course of the surface tension values was measured on a CBVP-Z automatic tensiometer (Kyowa Ltd., Japan).

Biodegradation Test

Biodegradation test was conducted according to JIS K-6950 for the evaluation of biodegradation of plastics using active sludge. Biological oxygen demand (BOD) was measured using a BOD Tester (TAITEC Co. Ltd., Tokyo, Japan). Aniline was used as a reference material for this test.[11] BOD and biodegradability were calculated by the following equation:

$$\mathrm{BOD}(\mathrm{mg\,L^{-1}}) = \frac{32 \times A}{0.082 \times 298} \times \frac{1000}{200}$$

where 32 is the molecular mass of oxygen, A is the consumption of oxygen (mL), 0.082 is the gas constant ($\mathrm{atm \cdot L \cdot mol^{-1} \cdot K^{-1}}$), 298 is the measurement temperature (K), and 200 is the volume of test water (mL).

Biodegradation of sample [(D_B (%)] was estimated from the theoretical biological oxygen demand (ThOD).

$$D_B = \frac{S - B}{\mathrm{ThOD}} \times 100$$

where S is the BOD of biotic test broth (mg), B is the BOD of biotic blank test broth (mg), and ThOD is the calculated value of consumption of oxygen necessary to oxidize the sample completely (mg). ThOD was calculated by the following equation for the compound without nitrogen. The composition formula ($C_cH_hO_o$) was calculated on the basis of elemental analysis.

$$\text{ThOD(mg)} = \frac{A \times M_o \times (2c + (h - 3n)/2 - o)}{c \times M_c + h \times M_h + n \times M_n + o \times M_o}$$

where A is the weight of sample (mg), and M_c, M_h, M_n and M_o are the atomic masses of carbon, hydrogen, nitrogen and oxygen, respectively.

General Analysis

The average molecular mass of amphiphilic lignin derivatives was measured by Shimadzu GPC system (Prominence LC) with Shodex KD-806M columns and DMF/0.1M LiCl as an eluent. UV and RI detectors were used, and the system was calibrated using polystyrene standards. FTIR spectra were recorded on a ThermoFisher Nicolet6700 FTIR by using the diffuse reflectance method. Sample concentration was adjusted at 5% (KBr dilution), and a scan number of 128 and spectral resolution of 4.0 cm^{-1} were employed. NMR measurement was performed on a JEOL 270-MHz spectrometer.

RESULTS AND DISCUSSION

Preparation and Characterization of Lignin Amphiphile (PEGDE-AL)

In our previous method,[6] it took three days to prepare the lignin amphiphile, which would be too long for commercial production. In this study, we attempted to explore more suitable reaction conditions to prepare the lignin amphiphile for the surfactant application. The amphiphilicity of lignin derivatives was verified by their water solubility. When PEGDE with $n \geq 9$ of the ethylene oxide (EO) repeating units was used, water solubility of AL derivatives (PEGDE-AL) increased with increasing PEGDE charge. However, no amphiphilicity was observed in PEGDE-AL by the use of PEGDE with $n = 1$ even though a large amount of PEGDE was charged. AL could be converted to amphiphiles by 2 h reaction at 70°C by charging more than equal amounts of PEGDE having $n \geq 9$ of EO repeating unit. Using these conditions we were able to shorten the reaction time with a small amount of epoxide compounds.

FT-IR spectrum showed an increase in the ν_{C-O} band, suggesting the presence of PEG moiety in AL (data not shown). The content of EO unit in PEGDE-AL was determined by the modified Morgan method[8,9] to estimate the hydrophilic-lipophilic balance (HLB) as an indication of surfactants. Table 1 shows EO content, HLB, and molecular mass of the lignin derivative, where the first and second numbers in parenthesis are the number of EO repeating unit (n), and the weight ratio of PEGDE to AL, respectively. The EO content was

Table 1. Chemical characteristics and surface activity of lignin amphiphiles prepared in this study

Entry		EO (%)	PEG (mol/AL1mol)	HLB	Mn	Mw/Mn	Surface tension (mN/m)	CMC (g/L)
1	PEGDE AL (9, 1)	54.9	4.5	11.0	22,700	8.3		
2	PEGDE AL (9, 1.5)	57.5	5.0	11.5	26,300	7.9	43	6.2
3	PEGDE AL (9, 2)	61.6	6.0	12.3	31,600	7.4	42	12.0
4	PEGDE AL (9, 2.5)	69.0	8.3	13.8	18,500	5.9	42	13.0
5	PEGDE AL (9, 3)	69.8	8.6	14.0	38,200	7.1	42	13.0
6	PEGDE AL (9, 4)	72.3	9.7	14.5	45,200	6.3	40	13.0
7	PEGDE AL (13, 1)	61.2	4.3	12.2	21,100	10.6	45	6.3
8	PEGDE AL (13, 1.5)	58.2	3.8	11.6	—	—	42	12.0
9	PEGDE AL (13, 2)	68.9	6.0	13.8	27,300	8.3	41	25.0
10	PEGDE AL (22, 1)	61.8	2.8	12.4	20,800	10.9	44	6.3
11	PEGDE AL (22, 2)	70.1	4.0	14.0	23,800	8.9	41	25.0
12	PEGDE AL (9, 2.5)	68.0	8.7	13.6	—	—	43	6.5
13	PEGDE AL (13, 2)	63.8	5.1	12.8	18,300	6.9	42	3.2
14	PEGDE AL (13, 3)	67.0	5.9	13.4	26,300	12.8	36	50.0
15	PEGDE AL (13, 4)	72.3	7.6	14.5	24,000	6.0	36	50.0
16	PEGDE AL (22, 2)	61.8	2.9	12.4	15,700	8.8	42	3.2

In parenthesis, the first value is the number of EO repeating unit of the used epoxy compounds, and the second one is a charge ratio of epoxy compound to AL. EO is weight percent of EO repeating unit (PEG moiety) in lignin amphiphiles. PEG is molar ratio of EO unit to AL.

HLB is hydrophile-lipophile balance calculated by the Griffin equation. Surface tension is at CMC.

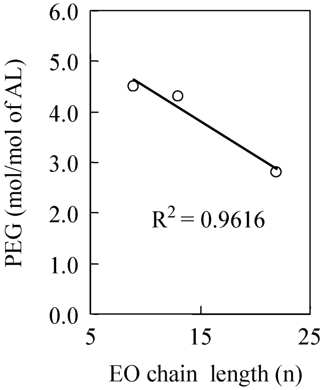

Figure 2. The linear relationship in the threshold charge ratio of PEGDE to AL to prepare water-soluble lignin derivative between the number of EO repeating unit at the minimum charge ratio of and the molar ration of PEG moiety in the lignin derivatives.

obviously increased with increasing PEGDE charge. When the number of EO units at the minimum charge ratio of PEGDE to prepare the water-soluble lignin derivative was plotted against the molar ratio of PEG moiety to AL (Figure 2), a linear relationship was observed. By extrapolation of the relation up to $n = 1$, most of hydroxyl groups in AL (more than 90%) needed to be reacted with epoxy group of PEGDE to obtain a water-soluble derivative. Accordingly, the reason why the water-soluble derivative could not be obtained with PEGDE with $n = 1$ was attributed to the low reactivity of hydroxyl groups in AL.

HLB value was calculated by Griffin's equation[12] based on the weight ratio of PEG moiety to AL moiety in PEGDE-AL. The HLB values of all PEGDE-AL were ranged from 11.0 to 14.5. This result suggests that PEGDE-AL was a promising surfactant for an oil-in-water (O/W) type emulsifier and a detergent if it has an adequate surface activity.

Surface Activity of PEGDE-AL

To examine the feasibility of PEGDE-AL to use as a surfactant, the surface tension of water in the presence of PEGDE-AL was measured by the ring method.[10] No depression of surface tension could be observed by the addition of AL and saponified AL due to their insoluble property in water. PEG dissolves in both water and organic solvents, such as chloroform and benzene. However, the depression of water surface tension by addition of PEG was very limited, and could not determine the CMC, as shown in Figure 3. In contrast, PEGDE-AL remarkably depressed the water surface tension. Surface tension-concentration

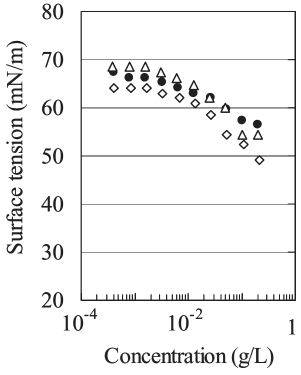

Figure 3. Surface tension-concentration isotherms for PEGDEs. △, PEGDE with $n = 9$ of EO unit; ●, PEGDE with $n = 13$; ◇, PEGDE with $n = 22$.

isotherms for PEGDE-AL preparations with $n = 9$ of EO unit are shown in Figure 4. Surface tension was decreased almost linearly by the addition of PEGDE-AL (entry 1 in Table 1) with low PEG content (Figure 4(A)). And those with higher PEG contents (entries 2–6) showed an inflection point on the isotherms, which corresponded to the critical micelle concentration (CMC). The CMC point was more clearly observed for PEGDE-AL with high PEG contents. The PEGDE-AL of entry 6 showed the lowest surface tension at CMC, 13.0 g/L. Because lignosulfonate, a commercial lignin surfactant, showed 46 mN/m of surface tension at 19.7 g/L of CMC, the PEGDE-AL of entry 6 has stronger surface activity in smaller concentrations than lignosulfonate.

As PEG and PEGDE did not show significant surface activity, the surface activity of the PEGDE-AL was attributed to the hydrophobicity of lignin. In comparison of CMC of PEGDE-AL having the same EO chain length, the lowest CMC was observed for the PEGDE-AL having the lowest EO content. On the other hand, the lowest surface tension was observed for the PEGDE-AL having the highest EO content.

The isotherm for PEGDE-AL did not take plateau state in the higher concentration ranges of CMC, while Triton® X-100, a commercial surfactant with low molecular mass, took the constant surface tension values (Figure 5). In general, it takes a long period to reach equilibrium state of surface tension for macromolecular surfactants.[13] Therefore, this different observation between PEGDE-AL and Triton® X-100 would suggest that the measurement of surface tension with the PEGDE-AL was not performed at the equilibrium state. Hence, time courses of surface tension in the presence of PEGDE-AL (entry 7) at CMC and its half concentration were followed by using the automatic tensiometer, as shown in Figure 6. The surface tension using the lignin amphiphile dramatically decreased with prolonged time, while that using Triton® X-100 slightly

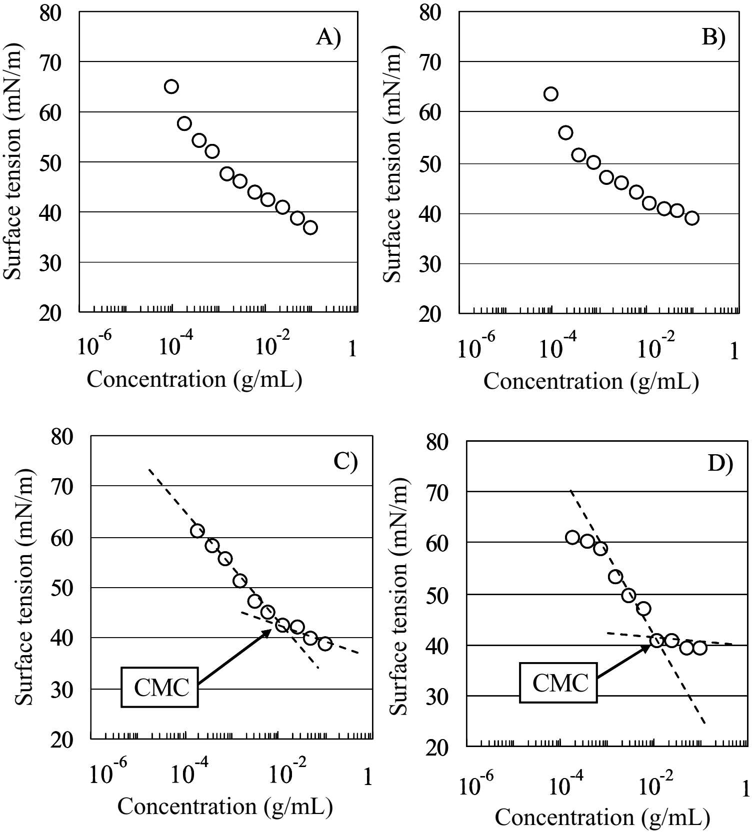

Figure 4. Surface tension-concentration isotherms for PEGDE-AL preparations with $n = 9$ of EO unit. A), entry 1; B), entry 3; C), entry 5; D), entry 6. Surface tensions at CMC are listed in Table 1.

decreased. However, the minimum surface tension using the lignin amphiphile was still higher than that using Triton® X-100.

Improvement of Surface Activity of AL Amphiphiles

Bifunctional epoxides, PEGDE, act as a crosslinker of AL molecules,[14] which would restrict the segmental motion of hydrophilic domain, thereby reducing the surface activity of PEGDE-AL. To avoid this undesirable crosslinking reaction, PEGDE was converted to monofunctional epoxides, EPEGGE, by blocking an epoxide group at one end with an ethoxyl group. To prepare water-soluble AL derivatives by the reaction with EPEGGE, a twofold amount of

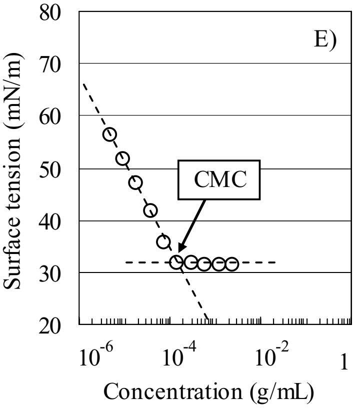

Figure 5. Surface tension-concentration isotherm for TritonX-100. CMC and surface tension at CMC were 0.15 g/L and 32 mN/m, respectively.

EPEGGE was required as compared with the corresponding PEGDE due to the fact that EPEGGE has only one reaction site and therefore lower reactivity than PEGDE. The HLB values of the resultant EPEGGE-ALs were also in the range of 11–14.5.

EPEGGE-AL depressed the surface tension of water [Figure 7(F) and (G)]. The EPEGGE-AL of entry 13 exhibited the lowest CMC among all the lignin derivatives prepared in this study, although the surface tension was in the similar level with those of PEGDE-AL. In addition, the lignin amphiphiles of entry

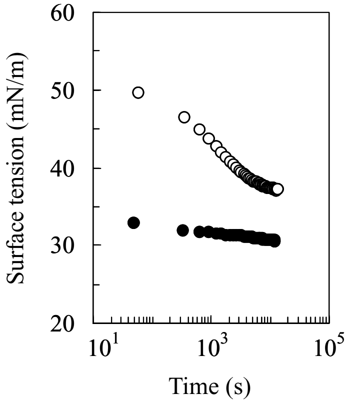

Figure 6. Time course of the water surface tension after the addition of PEGDE of entry 7 (○) and TritonX-100 (●).

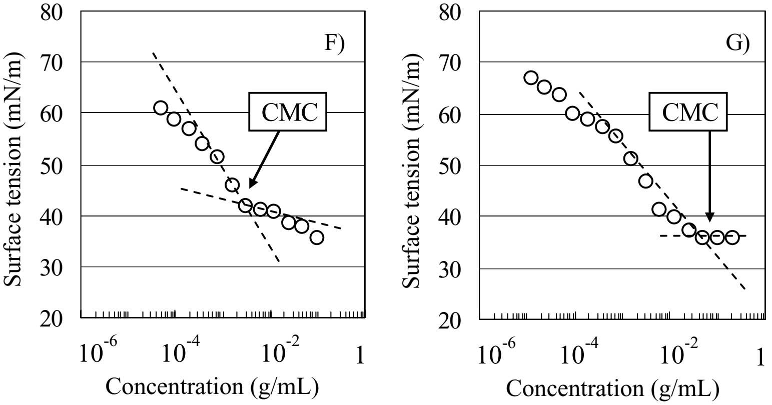

Figure 7. Surface tension-concentration isotherms for EPEGGE-AL preparations with $n = 13$ of EO repeating unit (entry 13, F) and with n = 22 (entry 15, G). The surface tensions at CMC are listed in Table 1.

14 and 15 brought about much lower surface tension (36 mN/m) than did the corresponding PEGDE-AL of entry 9, and the value was the lowest. Figure 8 shows time course of surface tension in the presence of EPEGGE-AL (entry 15). In the equilibrium state, the surface tension at the CMC reached 28 mN/m, which was lower than that using Triton® X-100. Thus, the surface activity of the lignin amphiphile could be improved by using mono-epoxy PEG derivative with long EO units.

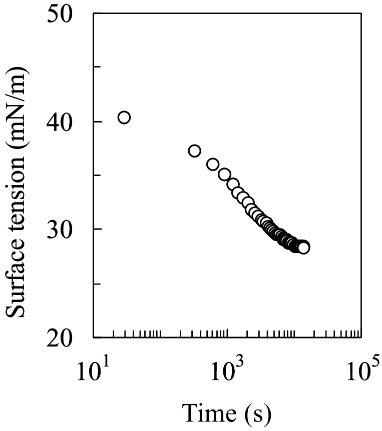

Figure 8. Time course of the surface tension after the addition of EPEGGE-AL of entry 15.

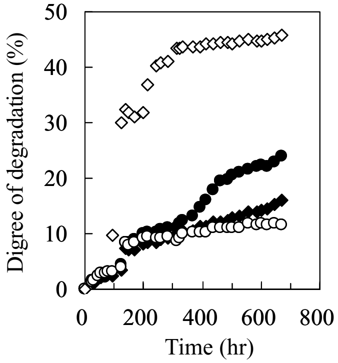

Figure 9. Biodegradation of PEGDE-AL of entry 7 (●), AL (△), KL (○), and aniline (◇) as a reference.

Biodegradability of Amphiphilic Lignin Derivatives

In general, surfactants are required to have biodegradability, because they are discharged into the living environment, such as sewage. The biodegradability of lignin amphiphiles was evaluated according to JIS K 6950. In this test, aniline was used as a control to determine the activity of active sludge. The lignin amphiphile was degraded in two steps. Future study will be required for the in-depth consideration of biodegradability of lignin amphiphiles. However, it is evident that the amphiphile lignin has higher biodegradability in comparison with the isolated lignins, such as AL and soft wood kraft lignin (Figure 9).

CONCLUSION

Lignin amphiphiles having 10–14 HLB values were firstly prepared with commercially available PEGDEs having various EO repeating units in a shortened preparation process. The resultant lignin amphiphiles had good surface activity and considerably depressed the surface tension of water, although the surface activity of PEGDEs was limited. Surface activity of lignin amphiphiles must be caused by the action of AL as a hydrophobic domain and PEGDE as a hydrophilic domain. However, the surface tension at CMC was higher for AL amphiphiles in comparison with a commercial nonionic surfactant, Triton® X-100. This inferior surface activity could be attributed to the crosslink of AL by PEGDE.

To improve surface activity, lignin amphiphiles were prepared using monoepoxy PEG derivatives. The resultant EPEGGE-AL had excellent surface activity in comparison with Triton® X-100. The surface tension of water could be depressed to 28 mN/m by the addition of EPEGGE-AL at CMC concentration in the equilibrium state, which was lower than that for Triton® X-100, 31 mN/m.

The biodegradability of the lignin amphiphiles was confirmed by the biodegradation test using active sludge. Consequently, the amphiphilic lignin prepared in this study could be utilized as surfactants that are used as detergents and emulsifiers.[15,16]

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