Enhanced Propoxylation of Alcohols and Alcohol Ethoxylates[1]

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ABSTRACT: An alkoxylation catalyst consisting of a calcium/aluminum complex partially neutralized in an alcohol ethoxylate base was found to be substantially more active than a conventional potassium hydroxide catalyst in the propoxylation of alcohols and alcohol ethoxylates. With the Ca/Al alkoxide catalyst, propoxylation was faster, required less catalyst, and proceeded at lower temperatures. The latter is desirable since it could help reduce the formation of allyl alcohol and allyl alcohol propoxylate by-products. The two catalysts produced different oligomer distributions, particularly at higher temperatures, which were found to have a marginal impact on surface chemistry.

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Alcohol propoxylates and alcohol ethoxylate/propoxylates are used in a variety of applications, most notably as co-monomers in condensation polymerization and as lower-foaming surfactants. Unlike ethylene oxide, propylene oxide adds hydrophobicity and steric bulk because of methyl branching that occurs during oligomerization. The impact of polypropylene oxide on performance properties has been discussed elsewhere (1).

Like ethoxylation, propoxylation can be achieved using a conventional catalyst, usually potassium hydroxide (KOH), and conventional alkoxylation equipment. Propylene oxide, however, is less reactive than ethylene oxide. Although the reaction temperature can be increased to compensate for lower reactivity, increasing reaction temperature also increases by-product formation. As shown in Scheme 1, KOH reacts with propylene oxide to form an unsaturated alkoxide (allyl alkoxide) salt (2). After further propoxylation and neutralization, allyl alcohol and allyl alcohol propoxylates are produced. These by-products are undesirable because they reduce the yield of the desired product and, because of unsaturation, they can interfere with polymerization. Consequently, propoxylations are typically performed under mild conditions (around

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125°C), require high catalyst levels (thousands of ppm), and take hours instead of minutes to complete.

This paper compares the influence of catalyst concentration and reaction rate of two catalysts, KOH and a calcium (Ca)/aluminum (Al) alkoxide complex, on reaction rate, reaction temperature, and oligomer distribution. Because a safe and reliable analytical method is not available at our site for accurately measuring allyl by-product concentrations, we assumed that by-product formation is directly related to temperature and to catalyst level and is independent of catalyst composition.

Although this study compares KOH to a Ca/Al alkoxide complex catalyst, other ethoxylation catalysts based on barium, lanthanum, magnesium, and the like may also be effective propoxylation catalysts.

EXPERIMENTAL PROCEDURES

Alkoxylation catalysts. Propoxylations and ethoxylations were performed with KOH and with an alkoxylation catalyst complex (called NOVEL® II; CONDEA Vista Company, Houston, TX) that consists of a Ca/Al complex partially neutralized in an alcohol ethoxylate base (3). This Ca/Al alkoxide catalyst is an effective ethoxylation catalyst for producing "peaked" or "narrow-range" alcohol ethoxylates, and for the ethoxylation and propoxylation of esters (4–9).

Alkoxylations. Alkoxylations were performed in a conventional 400-mL stainless steel autoclave (fabricated in-house) equipped with a magnetic stirring bar, an internal cooling line, and a thermocouple to monitor reaction temperature. Each reactor was contained in an insulated heating block. Temperature was monitored, and heat controlled by an I^{2}R (Cheltenham, PA) Therm-O-Watch model TCP3-1200 temperature controller. Compressed air was used for cooling and was controlled by an I^{2}R Therm-O-Watch model L9-1500 RTD controller. A 500-mL bomb containing the alkylene oxide under 50 pounds of N$_2$ pressure was connected in parallel with a graduated site-glass and connected to the autoclave *via* stainless steel tubing.

The experimental procedure consisted of six steps: (i) charging the propylene oxide (PO) (or ethylene oxide) reservoir, (ii) charging the reactor with feedstock, (iii) stripping the reactor with nitrogen to remove moisture, (iv) adding of alkoxylation catalyst followed by nitrogen stripping, (v)
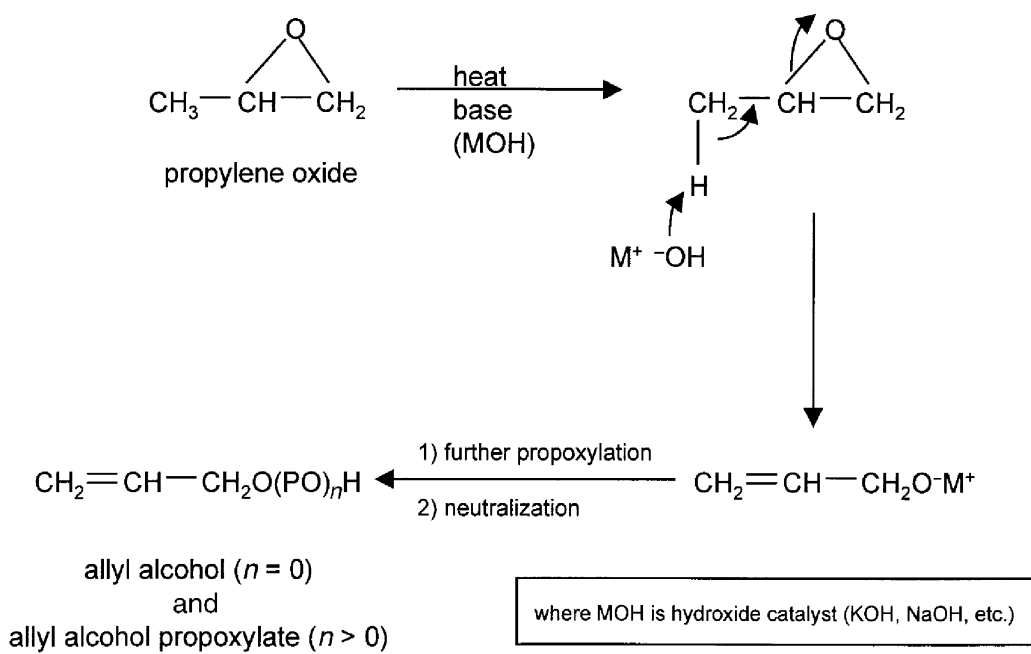
SCHEME 1

adding alkylene oxide to the feedstock, and (vi) allowing the PO to react until a constant pressure was observed.

Distribution of oligomers. The term "oligomer" (or poly-oxypropylene oligomer) is used to define a molecule containing one or more polymeric units of PO. The distribution of oligomers refers to the relative concentration (in wt%) of 0-mol oligomer (unpropoxylated feedstock), 1-mol oligomer, 2-mol oligomer, 3-mol oligomer, and so on.

The level of free alcohol (unpropoxylated alcohol) remaining in the product was determined by gas chromatography (GC) as follows: 20 mg of sample was mixed with 1 mg of 1-nonanol (Aldrich, Milwaukee, WI) as an internal standard; the mixture was then derivatized with Tri-Sil® Reagent (Pierce Chemical Company, Rockford, IL) to obtain trimethyl silyl ethers. One microliter of derivatized sample + standard was then injected into a Varian (Sunnydale, CA) model 3400CX gas chromatograph equipped with a flame-ionization detector and a Supelco (Bellefonte, PA) 10% methyl silicone 6' by 0.125" o.d. column. Temperature was ramped at 6°C/min from 80 to 300°C, and held at 300°C for 20 min.

Oligomer distributions were determined with a Hewlett-Packard (Avondale, PA) model 5890 gas chromatograph equipped with a Hewlett-Packard hydrogen flame detector (model 5890), and a 30-m (0.32" i.d.) J&W Scientific (Folsom, CA) DB-1 dimethylpolysiloxane column. Temperature was ramped as follows: initial temperature = 90°C/final temperature = 310°C/rate = 5°C/minute.

Oligomer distributions of test ethoxylate/propoxylates could not be obtained because of the large number of possible homologs which can be present (i.e., the ethoxylate homolog has its own distribution of oligomers, making

separation and identification impossible). To circumvent this problem, propoxylates were prepared using a monodisperse 6-mol ethoxylate (no other ethoxymers). The source of the pure 6-mol ethoxylate is discussed below.

Surface properties (Gibbs' plots). Gibbs' plots of surface tension vs. surfactant concentration were obtained using a Lauda Automated Tensiometer (Model TEIC distributed by Brinkmann, Westbury, NY). To maintain the same ionic strength for water, all test solutions contained 0.01 molar sodium sulfate.

Feedstocks. Two alkoxylation feedstocks were used: dodecanol (ALFOL 12 alcohol; CONDEA Vista Co., Houston, TX) and a pure 6-mol ethoxylate of *n*-dodecanol (hexaethyleneglycol mono *n*-dodecyl ether; Nikko Chemicals Co., Ltd., Tokyo, Japan).

RESULTS AND DISCUSSION

Propoxylation of linear alcohols. Reaction time and oligomer distribution were examined as a function of catalyst loading and reaction temperature in the preparation of both 2-mol (average) and 4-mol (average) propoxylates. Results are shown in Table 1.

As shown in Figure 1 and by data in Table 1, significantly shorter reaction times are obtained with the Ca/Al alkoxide catalyst. The relationship between temperature and reaction rate is also clearly different between the two catalysts. With KOH, reactivity clearly increases with increasing temperature, but with the Ca/Al alkoxide catalyst, reaction temperature has a smaller impact. With the 4-mol propoxylates, increasing reaction temperature increased reaction time.

TABLE 1
Impact of Catalyst Loading and Reaction Temperature on Reaction Time for 2-Mol and 4-Mol Propoxylation of Dodecanol Using KOH and Ca/Al Alkoxide Catalysts

Product[a]	Catalyst	Catalyst Loading (g catalyst/g of total batch)[b,c]	Catalyst (metal ion) concentration (ppm)	Reaction temperature (°C)	Reaction time (min)[d]
C_{12}-2 PO	KOH	1.13/300	2612	125	110
	KOH	1.13/300	2612	100	240
	KOH	1.13/300	2612	85	240
	Ca/Al alkoxide[b]	2.00/300	225	125	61
	Cal/Al alkoxide[b]	2.00/300	225	100	48
	Ca/Al alkoxide[b]	2.00/300	225	85	65
C_{12}-4 PO	KOH	0.56/300	1307	125	<250
	KOH	1.13/300	2612	125	174
	KOH	1.13/300	2612	100	>300
	Cal/Al alkoxide[b]	4.00/300	450	125	85
	Ca/Al alkoxide[b]	4.00/300	450	115	<63
	Ca/Al alkoxide[b]	4.00/300	450	100	60
	Ca/Al alkoxide[b]	4.00/300	450	85	<50
	Ca/Al alkoxide[b]	2.00/300	225	85	<50
	Ca/Al alkoxide[b]	4.00/300	450	75	<39
	Ca/Al alkoxide[b]	2.00/300	225	75	<120

[a]Mols PO are the average number of mols PO added.
[b]See Reference 3.
[c]g of catalyst (100% active basis) used to prepare propoxylate.
[d]Time to incorporate PO as measured by observing the drop in PO pressure until there was no further decrease in reactor pressure [i.e., soaking down PO in gas cap; times that are "<" (or "less than") some value indicate that insufficient cooling was available during the reaction, such that PO addition had to be controlled; times that are ">" (or "more than") some value indicate that pressure was dropping slowly, and that operator made a "best guess" as to when the reaction was complete; times are approximate].

The difference in reactivity of the two catalysts results from differences in their propoxylation mechanisms. As shown in Figure 2A, KOH first forms potassium alkoxide as the active intermediate (Step A) which then reacts with PO to form the oligomer (Step B). Steps A and B are also the first two steps in the proposed mechanism by which the Ca/Al alkoxide catalyst operates (see Fig. 2B). However, because the catalyst metals are multivalent, we believe the catalyst can also complex with PO (Step C), making it more susceptible to nucleophilic attack by both the parent alcohol and the alkoxide. This additional pathway results in greater reactivity for the Ca/Al alkoxide catalyst. At any given temperature, reaction times are therefore reduced significantly.

The greater reactivity of the Ca/Al alkoxide catalyst also has an advantage in terms of catalyst loading. Propoxylations with KOH typically utilize more than 2,000 ppm of catalyst (on an active metal ion basis) to achieve reaction in a reasonable length of time. With the Ca/Al alkoxide catalyst, however, between 200 and 500 ppm of active catalyst appears to be more than adequate to achieve high reactivity. This unique low-temperature phenomenon may be a manifestation of step C in the mechanism illustrated in Figure 2B. Here, the overall reaction rate may be proportional to the PO concentration raised to a power greater than one. Thus, the effect of higher PO concentration at lower temperatures may more than counterbalance the natural retardation of the reaction rate as temperature is decreased.

The fact that the Ca/Al alkoxide catalyst achieves reaction under milder conditions is significant. Typically, KOH-catalyzed propoxylations are run at approximately 125°C and last hours instead of minutes. Although higher reaction temperatures reduce reaction time, they also lead to greater by-product formation. Consequently, reaction conditions for KOH-catalyzed propoxylations are more or less fixed, representing a balance between the need to minimize production time and the need to minimize by-product formation. The Ca/Al alkoxide catalyst provides a significant shift in this balance, allowing shorter reaction times at lower reaction temperatures and lower catalyst levels.

Oligomer distributions (relative concentrations of unpropoxylated feedstock, 1-mol propoxylate, 2-mol propoxylate, and so on) for the 2-mol (average) propoxylates are shown in Figure 3A, B. The two catalysts yield distinctly different oligomer distributions. Surprisingly, as one can see by comparing Figure 3A with 3B, the KOH-catalyzed propoxylate has a slightly more "peaked" distribution than its Ca/Al alkoxide catalyst counterpart. However, the KOH-catalyzed propoxylates also have a significant concentration of unpropoxylated feedstock (0-mol homolog), whereas the complex-catalyzed propoxylates all have less than 0.3% unpropoxylated feedstock. This supports the premise that the relative reactivity of unpropoxylated feedstock is greater with the Ca/Al alkoxide catalyst, as depicted by step C in Figure 2B. This phenomenon is reminiscent of acid-catalyzed alkoxylations.
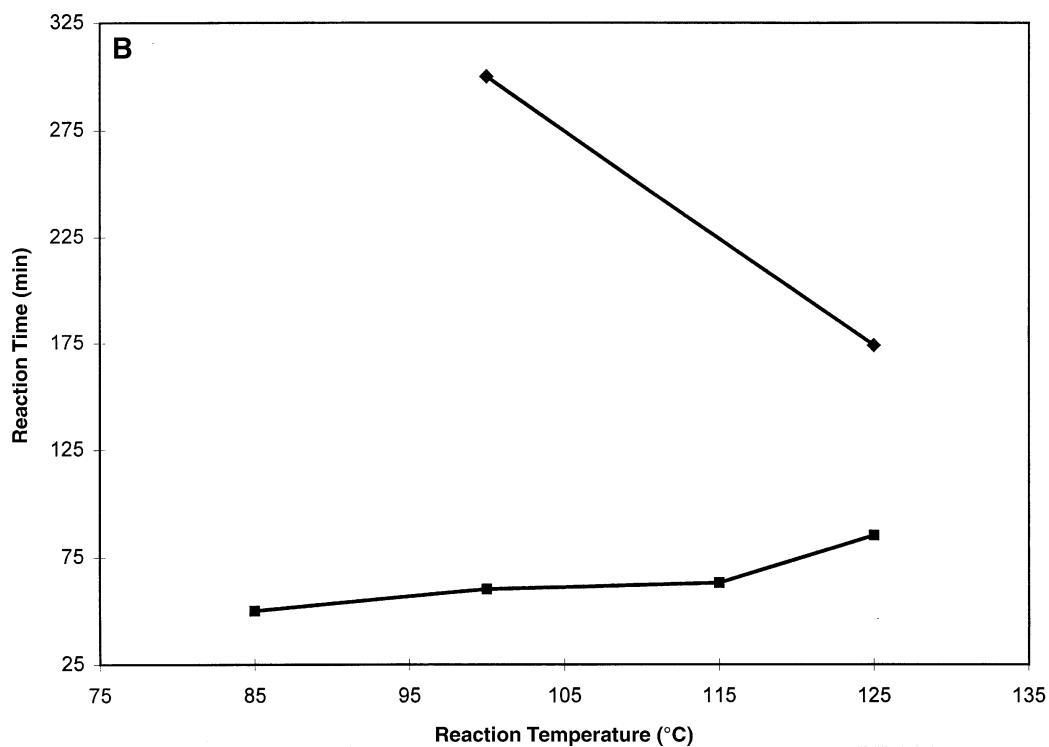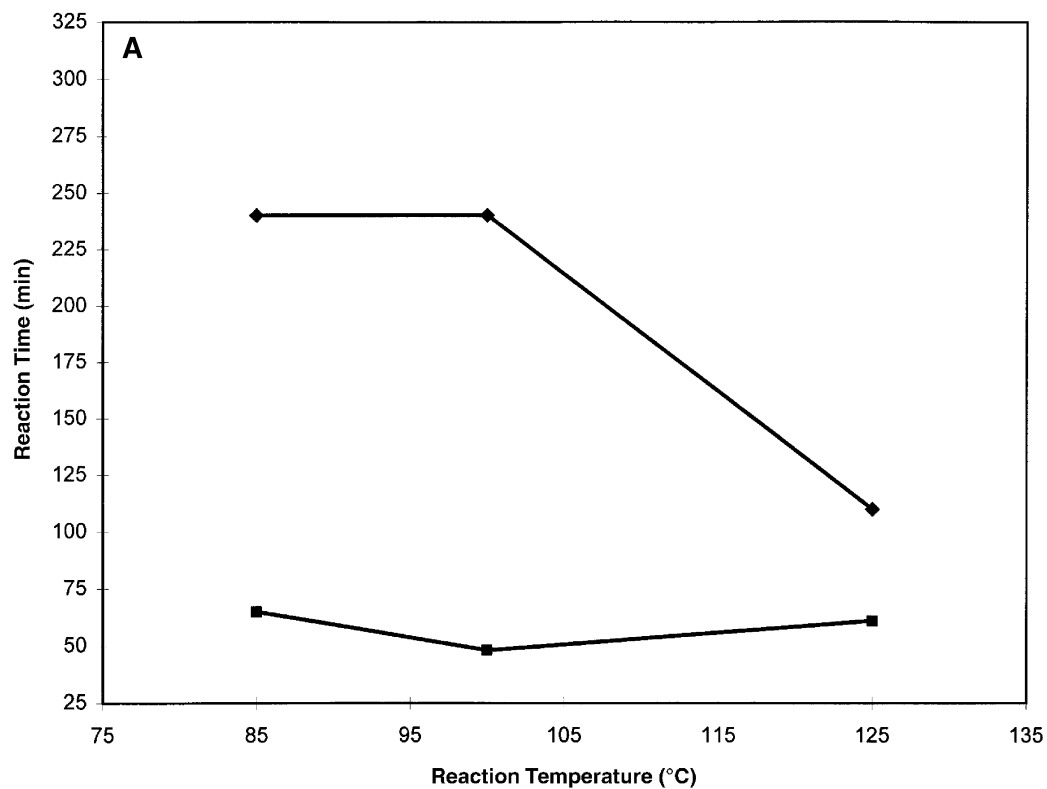
FIG. 1. Impact of reaction temperature on reaction time [time to incorporate propylene oxide (PO)] for preparation of (A) 2-mol propoxylates and (B) 4-mol propoxylates of dodecanol using potassium hydroxide (KOH) (◆, 2612 ppm active catalyst) and calcium/aluminum (Ca/Al) alkoxide catalysts [■: (A) 225 ppm active catalyst and (B) 450 ppm active catalyst].
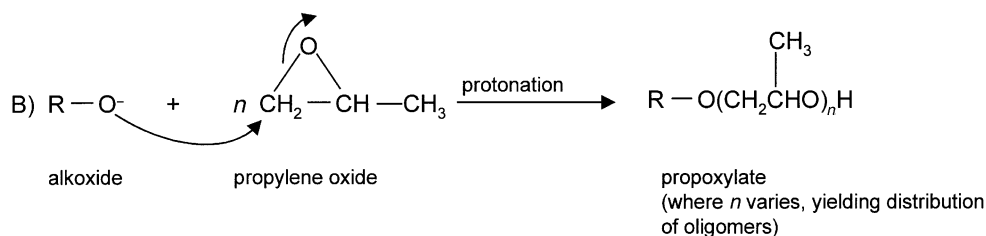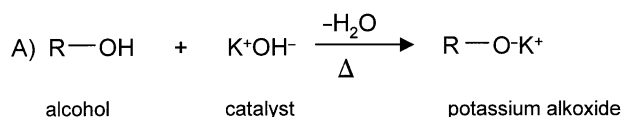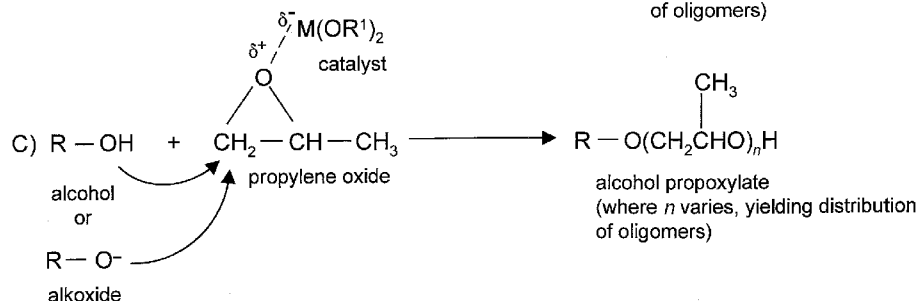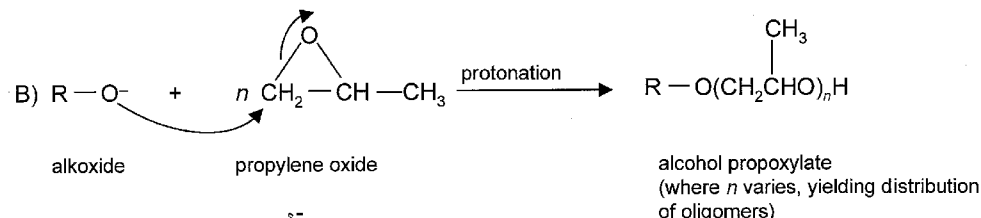
A Conventional Catalyst (KOH)

A) $R—OH$ + K^+OH^- $\xrightarrow[\Delta]{-H_2O}$ $R—O^-K^+$

alcohol   catalyst   potassium alkoxide

B) $R—O^-$ + n $CH_2—CH—CH_3$ (O) $\xrightarrow{protonation}$ $R—O(CH_2CHO)_nH$ (CH_3)

alkoxide   propylene oxide   propoxylate
(where n varies, yielding distribution
of oligomers)

B Catalyst Complex (NOVEL® II)

A) $2R—OH$ + $M(OR^1)_2$ $\xrightarrow{\Delta}$ $(R—O)_2M + R'OH$

alcohol   NOVEL® II   NOVEL® II   alcohol
                 catalyst   ethoxylate

B) $R—O^-$ + n $CH_2—CH—CH_3$ (O) $\xrightarrow{protonation}$ $R—O(CH_2CHO)_nH$ (CH_3)

alkoxide   propylene oxide   alcohol propoxylate
(where n varies, yielding distribution
of oligomers)

δ^- $M(OR^1)_2$ catalyst
δ^+ O

C) $R—OH$ + $CH_2—CH—CH_3$ $\longrightarrow$ $R—O(CH_2CHO)_nH$ (CH_3)

alcohol   propylene oxide   alcohol propoxylate
or   (where n varies, yielding distribution
                                           of oligomers)
$R—O^-$
alkoxide

FIG. 2. Mechanism for propoxylation of alcohols using (A) KOH catalyst and (B) Ca/Al. See Figure 1 for abbreviations. NOVEL® II, CONDEA Vista Company, Houston, TX.

As shown in Figure 3A and 3B, the PO distribution curve obtained with each catalyst at 100°C is less "peaked" than curves obtained at 125 and 85°C. The reason for this trend is not understood, but is not thought to be a result of variability in the analytical procedure to obtain the distribution.

Propoxylation of linear alcohol ethoxylates. The Ca/Al alkoxide catalyst was also compared to KOH in terms of its ability to propoxylate alcohol ethoxylate. The impact of catalyst concentration and reaction temperature on reaction time was examined using two ethoxylate feedstocks. One feedstock was 6-mol (average, by weight) dodecanol ethoxylate produced using the same catalyst intended for propoxylation. The second feedstock consisted of pure 6-mol ethoxylate of dodecanol (no other ethoxylate homologs). Results are listed in Table 2.

As shown in Figure 4 and data in Table 2, reaction times were again significantly shorter with the Ca/Al alkoxide catalyst than with KOH.

Oligomer distribution of the propoxylates made from the conventional ethoxylate could not be obtained because of the large number of ethoxylate/propoxylate homologs present. Distributions for propoxylates made from the pure 6-mol ethoxylate are shown in Figure 5A, B. With KOH, oligomer distributions are peaked in comparison to those obtained with the Ca/Al alkoxide catalyst. Comparison of Figures 5A and 5B shows that the degree of peaking appears to be most pronounced at the higher reaction temperature for both KOH and Ca/Al alkoxide catalyst in the propoxylation of dodecanol.

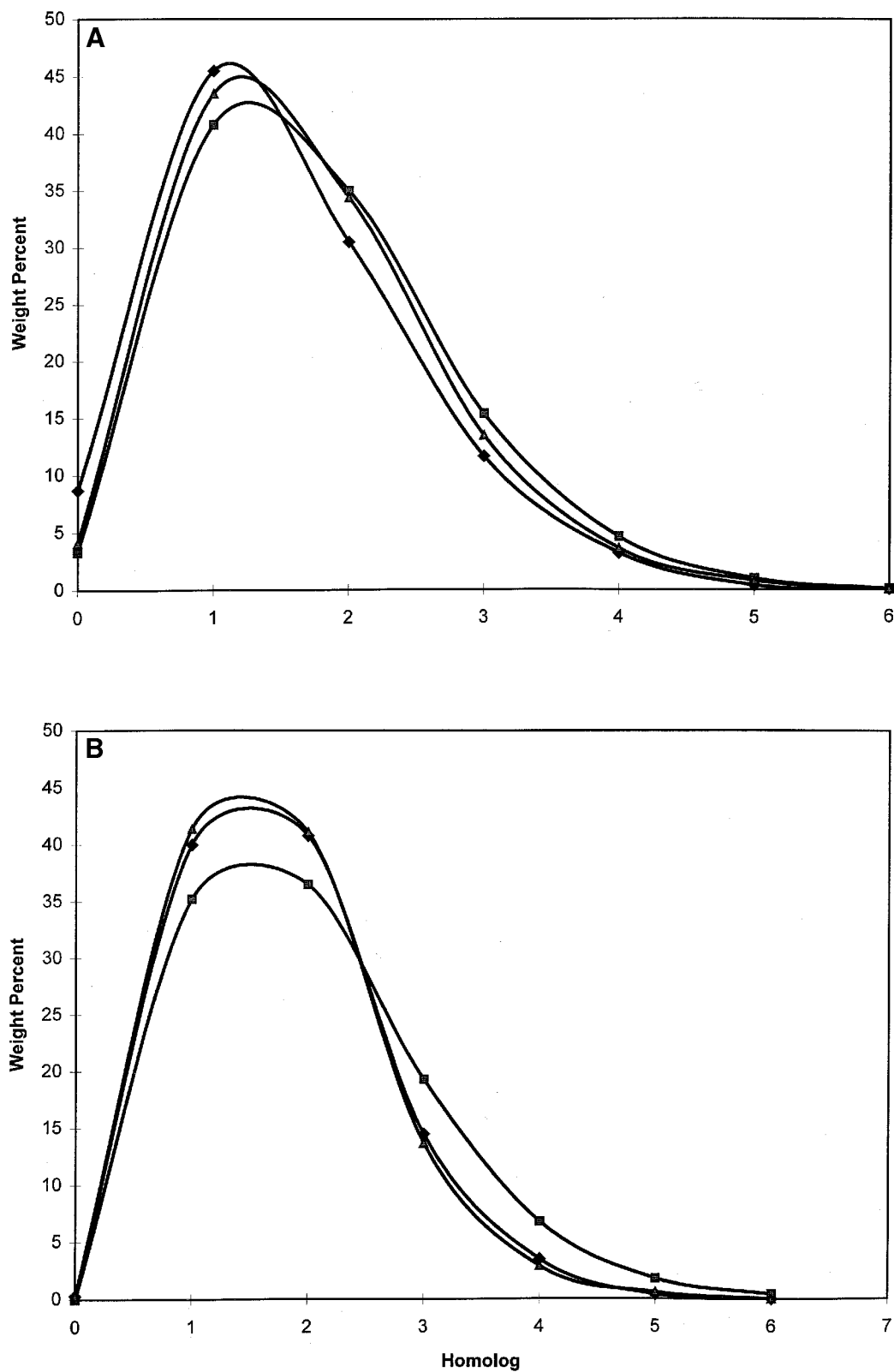Because some of the differences in oligomer distributions between the pure homolog and the mixed ethoxylate

FIG. 3. Oligomer distributions for dodecanol 2-mol propoxylates obtained with (A) KOH catalyst and (B) with Ca/Al alkoxide catalyst as a function of reaction temperature (◆, 125°C; ■, 100°C; ▲, 85°C). See Figure 1 for abbreviations.

TABLE 2
Impact of Catalyst Loading and Reaction Temperature on Reaction Time for the 2-mol Propoxylation of Dodecanol 6-mol Ethoxylate Using KOH and Ca/Al Alkoxide Catalysts

Feedstock	Product[a]	Catalyst	Catalyst loading (g/catalyst/g of total batch)	Catalyst (metal ion) concentration (ppm)	Reaction temperature (°C)	Reaction time (min)[b]
KOH-catalyzed 6-mol (avg.) ethoxylate of dodecanol	C_{12}-6 EO/2 PO	KOH	0.17[c]/300	397	125	>240
	C_{12}-6 EO/2 PO	KOH	0.17[c]/300	397	100	>240
Ca/Al alkoxide-catalyzed 6-mol (avg.) ethoxylate of dodecanol	C_{12}-6 EO/2 PO	Cal/Al alkoxide[d]	2.00[c]/300	225	125	120
	C_{12}-6 EO/2 PO	Ca/Al alkoxide[d]	2.00[c]/300	225	100	118
	C_{12}-6 EO/2 PO	Ca/Al alkoxide[d]	2.00[c]/300	225	80	>240
Pure 6-mol ethoxylate of dodecanol	C_{12}-6 EO[e]/2 PO	KOH	0.24/63	2612	125	100
	C_{12}-6 EO[e]/2 PO	KOH	0.24/63	2612	100	135
	C_{12}-6 EO[e]/2 PO	KOH	0.24/63	2612	85	210
	C_{12}-6 EO[e]2 PO	Ca/Al alkoxide[d]	0.84/63	450	125	60
	C_{12}-6 EO[e]/2 PO	Ca/Al alkoxide[d]	0.84/63	450	100	50
	C_{12}-6 EO[e]/2 PO	Ca/Al alkoxide[d]	0.84/63	450	85	75
	C_{12}-6 EO[e]/2 PO	Ca/Al alkoxide[d]	0.84/63	450	75	180

[a]Unless specified, mols of EO and PO represent the average number of mols added to feedstock by weight.
[b]Time to incorporate PO as measured by observing drop in PO pressure until there was no further decrease in reactor pressure (i.e., soaking down PO in gas cap); times that are ">" (or "more than") some value indicate that pressure was dropping slowly and that operator made a "best guess" as to when the reaction was complete; times are approximate.
[c]Catalyst added prior to preparation of alcohol ethoxylate; no additional catalyst added prior to propoxylation.
[d]See Reference 3.
[e]Hexaethyleneglycol mono n = dodecyl ether (purchased from Nikko Chemicals Co., Ltd, Tokyo, Japan).
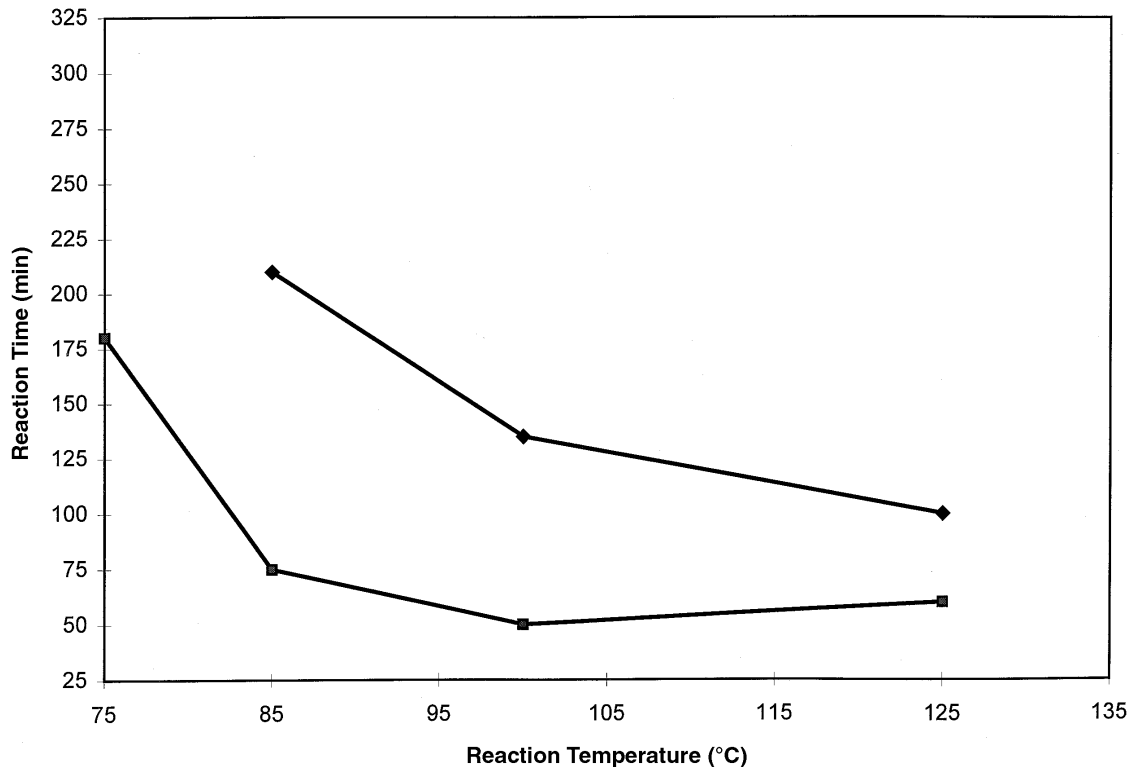

FIG. 4. Impact of reaction temperature on reaction time (time to incorporate PO) for preparation of 2-mol propoxylates from pure 6-mol ethoxylate of dodecanol using KOH (◆, 2612 ppm active catalyst) and Ca/Al alkoxide (■, 450 ppm active catalyst) catalysts. See Figure 1 for abbreviations.
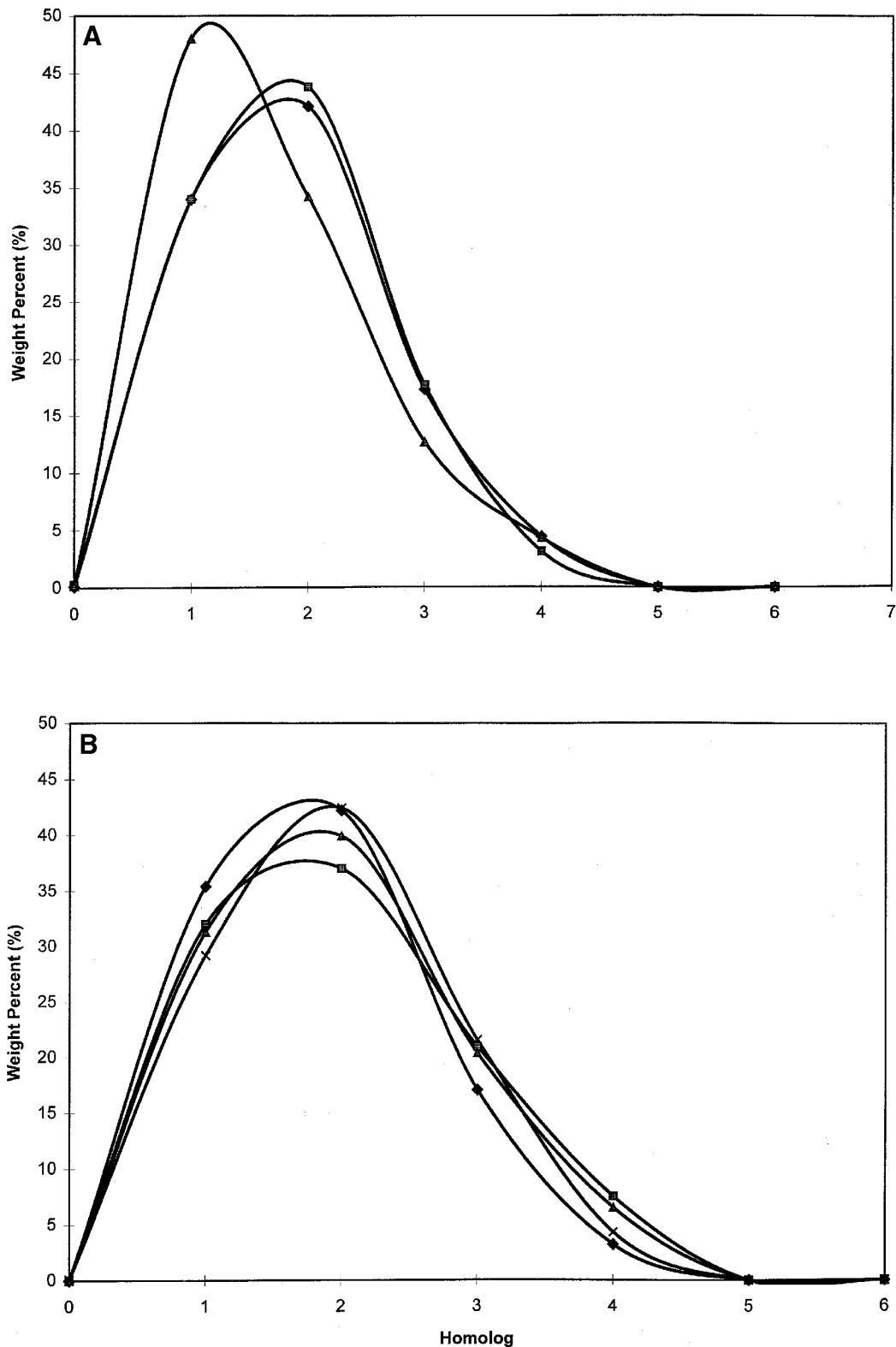
FIG. 5. Oligomer distributions for 2-mol propoxylates made from pure 6-mol ethoxylate of dodecanol using (A) KOH catalyst as a function of reaction temperature (◆, 85°C; ■, 100°C; ▲, 25°C) and (B) Ca/Al alkoxide catalyst as a function of reaction temperature (◆, 75°C; ■, 85°C; ▲, 100°C; X, 125°C). See Figure 1 for abbreviations.
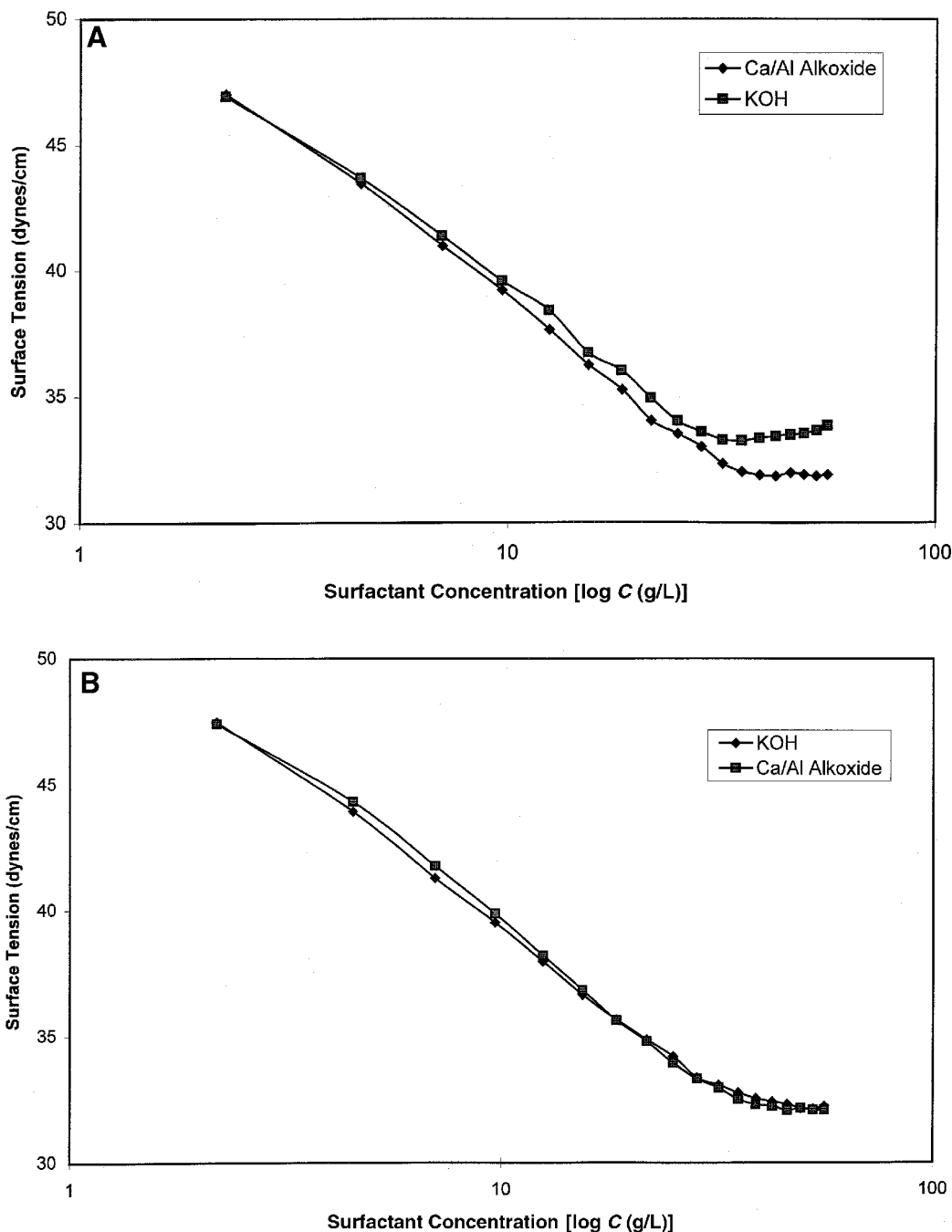
FIG. 6. Comparison of Gibbs' plots (surface tension vs. surfactant concentration) for 2-mol propoxylates made from pure 6-mol ethoxylate of dodecanol using KOH and Ca/Al alkoxide catalysts at (A) 125°C and (B) 85°C. See Figure 1 for abbreviations.

were quite pronounced, particularly at 125°C, Gibbs' plots (surface tension vs. surfactant concentration) were obtained to determine if these differences could affect surface chemistry. Results are given in Figure 6.

Gibbs' plots for the products propoxylated at 125°C clearly show a difference, particularly at surfactant concentrations above the critical micelle concentration (CMC). The propoxylate made with KOH has a surface tension of approximately 33.5 dynes/cm at its CMC (31.1 ppm),

while the propoxylate made with the Ca/Al alkoxide catalyst has a surface tension of 32.0 dynes/cm at its CMC (33.6 ppm). This suggests that a broader distribution of oligomers yields a more surface-active product. In contrast, Gibbs' plots for products propoxylated at 85°C are almost identical, corresponding with similar oligomer distributions (see Figs. 5A (◆) and 5B (■).

The differences in surface chemical properties discussed above are likely to prove marginal in practice. Moreover,

these ethoxylate/propoxylate products are unrealistic since they were derived from a pure 6-EO homolog. The results do show, however, that catalyst type affects oligomer distribution which, in turn, can impact surface chemistry.

ACKNOWLEDGMENTS

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