Alkoxylation of N-Alkyl Substituted Ethylenediamine[1]

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ABSTRACT

The alkoxylation of a new mixture of N-alkylethylenediamines obtained by reacting $C_{11.5\ av.}$ chloroparaffins and ethylenediamine was studied. Ethoxylation in both laboratory glassware or Parr autoclave equipment readily produced 20 mole adducts without alkaline catalysis. The reaction was initiated by the formation of the 3 mole adduct at 160 C and subsequent addition of the alkylene oxide at 90 C. The formation of adducts with mole ratios greater than 20 required an alkaline catalyst. The preparation of propoxylate derivatives necessitated the addition of 2.5-3.0 wt % of caustic catalyst. The preparative time was minimized by operating at 185-190 C and 40-50 psi. The surfactant properties of the alkoxylates were evaluated and correlated with structures and compositions. Data on solubility, surface tension, density, refractive index, pH and foam characteristics are presented. Polyurethane foams were prepared from several of the alkoxylates.
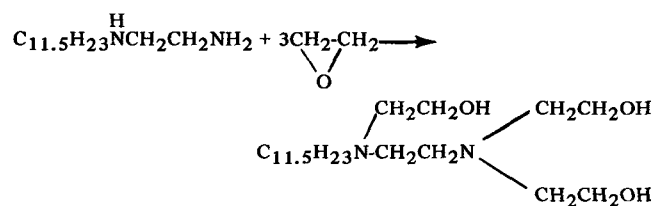
INTRODUCTION

Alkoxylated amines are a significant, although small, part of the commercial surfactant market. Their estimated annual volume is ca. 25-30 million lb., and the main applications are in corrosion inhibitor formulations and textile processing, and as emulsifiers in diverse specialty systems (1).

The preparation and reaction mechanisms of ethylene oxide additions to amines are well documented in the literature (2-4). Ethoxylations of linear alcohols, alkyl phenols and fatty acids normally require catalysis. Amines appear to undergo ethoxylation by a much more complicated mechanism, since each of the expected steps in the reaction sequence has a different set of optimum conditions. Komori and coworkers (5,6) and Sakakibara et al. (7) have studied these reaction steps with respect to temperature, induction period and effects of catalysis, and have concluded that the addition of catalysts is not required under certain reaction conditions. Further a high initial reaction temperature shortened the induction period, and a lower reaction temperature favored rapid ethoxylation after tertiary amines were formed. Sanders et al. (8) verified these results and showed that an in situ catalyst, a quaternary ammonium compound, is formed and gradually decomposes during continued alkoxylation. In addition, Stein and Umbach (9) were able to develop a continuous ethoxylation process for amine-ethylene oxide 1:6 utilizing the same principles.

Alkoxylation of di- and polyamino compounds has been reported (10-16), but little information is available on the preparation and properties of alkoxylates from alkyl-substituted ethylenediamine. It was decided to study a potentially available mixture of this type, Witcamine ED-14, a mixed $C_{11.5\ av.}$ paraffin-substituted ethylenediamine (16). Both the primary and secondary amino groups may be polyethoxylated after the formation of the initial 3-mole adduct:

$$C_{11.5}H_{23}NCH_2CH_2NH_2 + 3CH_2\text{-}CH_2 \longrightarrow$$

$$C_{11.5}H_{23}N\text{-}CH_2CH_2N \Big\langle {}^{CH_2CH_2OH}_{CH_2CH_2OH} , CH_2CH_2OH$$

The products produced were analyzed to determine total

TABLE I

Ethoxylation of Mixed N-alkylethylenediamines

		Reaction conditions				Product information		Calculated mol wt	
Run no.	Mole ratio, EO/amine	Pressure, psi	Catalyst	Reaction temperature, C	Reaction time, hr	Amine no.	Tert amine, %	Based on wt gain	Based on amine no.
1	3.1	atm	None	90-92	2.7	307	95.7	365	365
2	3.3	atm	None	160-165	1.1	312	96.2	356	360
3	3.4	atm	None	110	2.5	307	97.2	369	365
4	3.5	25	None	160-172	1.2	302	97.2	374	371
5	4.0	atm	None	100-110	2.9	286	98.1	396	392
6	5.2	atm	None	100-110	3.7	248	99.9	449	452
7	7.4	atm	None	95-100	4.2	209	100.0	545	537
8	7.6	atm	1% NaOH	100-102	4.1	206	100.0	554	545
9	9.5	atm	None	95-100	5.7	175	100.0	638	641
10	10.0	atm	1% naOH	100-102	5.8	171	100.0	660	656
11	15.8	atm	None	95-100	8.5	122	100.0	915	920
12	16.0	atm	1% NaOH	100-102	8.1	120	100.0	924	935
13	17.4	atm	None	100-110	12.0	111	100.0	986	1011
14	17.4	10-15	None	90-110	9.0	112	100.0	986	1002
15	17.8	atm	None	160-162 90-100	7.5	111	100.0	1003	1011
16	20.0	25	None	160-166 85-90	6.7	102	100.0	1100	1100
17	21.0	atm	None	90-94	14.5	99	100.0	1144	1133
18	24.6	atm	1% NaOH	90-94	21.5	84	100.0	1302	1336
19	28.6	atm	2% NaOH	160-170	19.8	77	100.0	1478	1457
20	48.7	40	3.2% NaOH	85-90	8.5	48	100.0	2363	2337

TABLE II

Propoxylation of Mixed N-alkylethylenediamines

Mole ratio, PrO/amine	Reaction time, hr	Catalyst, % NaOH	Temperature, C	Pressure, psi	Amine no. Found	Amine no. Calculated	Tert amine, %
3.2	1	2.3	180-200	40	279	280	75.1
3.9	1.2	2.3	185-195	35-40	251	254	84.9
12.0	15	2.4	180-200	atm	126.5	123	96.5
20.4	7.4	2.5	190-195	40	79.8	77.9	98.6
43	10.5	2.9	190-195	40	47.6	41.5	99.4

amine value, tertiary amine value and hydroxyl number. Surfactant properties were determined by a series of tests noted in the Experimental Procedures.

EXPERIMENTAL PROCEDURES

Materials

The ethylene oxide used in the reactions was a commercial grade initially used without further purification. Later on, in attempts to achieve more precise material balance relationships, the ethylene oxide was purified by a one plate distillation under a nitrogen atmosphere to remove polymeric and colored impurities which accumulated during tank storage. The ethylene oxide was transferred to a stainless steel cylinder and pressurized with 10 psi nitrogen for glassware experiments and 50-60 psi nitrogen for pressurized runs. A commercial grade of propylene oxide supplied by the Eastman Kodak Co. was employed without further purification.

Typical properties of the mixed N-alkylethylenediamines, which had been prepared from a mixture of C_9-C_{14} ($C_{11.5}$ av.) chloroparaffins having greater than 95% normal paraffin content and ethylenediamine, were: neutralization equivalent, 108-115; paraffin, 2-5%; chlorine, 1.5-2.5%; and water, 0.2-0.5%. The mixture was semiquantitatively determined to have minimal unsaturation. The amine contents were determined as 50% primary amine, 46% secondary amine and 4% tertiary amine. From gas chromatographic analysis the distribution of the ethylenediamino moiety along the paraffin chain was estimated to be 40-50% 1-substituted, 20-30% 2-substituted and 20-40% 3- and internally substituted.

Procedure

Ethoxylation. a) Atmospheric pressure in laboratory glassware: The apparatus for the reaction consisted of a 1 liter, four-necked flask equipped with heating mantle, thermometer, mechanical stirrer, nitrogen inlet, ethylene oxide inlet and a dry ice condenser protected by a $CaCl_2$ drying tube. The ethylene oxide cylinder was mounted on a scale so that the amount of ethylene oxide added could be followed by weight loss of the cylinder.

The amine was charged to a flask and preheated to 160 C under nitrogen. Ethylene oxide was metered at such a rate as to maintain 160 C with minimal reflux. After 2-2.5 moles of ethylene oxide had been added, as determined by weight loss of the cylinder, there was a moderate exotherm. Further reaction of the ethylene oxide proceeded very slowly. When the temperature was lowered, preferably to 90 C, ethoxylation proceeded more rapidly. A typical charge, 250 g of mixed N-alkylethylenediamines, took up ca. 100 g ethylene oxide per hour after the formation of the 3 mole adduct. After the desired amount of ethylene oxide was added, volatiles present in the product were removed from the reaction mixture under reduced pressure with a water aspirator.

b) Stainless steel system — pressure vessel: The apparatus for the reaction consisted of a 2 liter autoclave equipped with stirrer, thermometer, heating jacket, pressure gauge (0-100 psi), rupture disc (1000 psi), cooling coil and inlet tubing which was connected to the nitrogen and ethylene oxide cylinders. The weighed 1 liter cylinder, filled with ethylene oxide was pressurized to 50-60 psi with nitrogen and mounted on a scale. The autoclave and all auxiliary equipment were 316 stainless steel to preclude any catalytic effects from other materials.

The mixed N-alkylethylenediamines were charged to the autoclave, and the contents were flushed with nitrogen gas at least three times. The autoclave was heated to 160 C, and any nitrogen pressure developed during the heating was released. Ethylene oxide was then metered at a rate such that a pressure of ca. 25 psi was maintained. The temperature increase produced by the exotherm was not

TABLE III

Physical Properties of Ethoxylates

Run no.	Mole ratio, EO/amine	n_D^{25}	Density, g/cc	Cloud point, C 1% in Distilled H_2O	Cloud point, C 3% NaCl	Cloud point, C 10% NaCl
2	3.3	1.4828		26	8	1
4	3.5	---	0.975	---	---	---
5	4.0	1.4816		37	20	13
5A	4.6	1.4806		44	29	21
6	5.4	1.4803		57	42	32
7	7.4	---	1.011	---	---	---
10	10.0	1.4778[a]	1.025	97	83	67
11	15.8	1.4744		>100	100	80
13	17.4	---	1.052	---	---	---
17	21.2	1.4733		>100	>100	83

[a]10.9 EO.

TABLE IV

Surface Active Properties of Ethoxylates

Run no.	Mole ratio, EO/amine	0.1% Draves wetting sec	0.1% Surface tension (pH), dynes/cm		
2	3.3	45			
5	4.0	24	28.7 (9.9)	20.2 (7.0)	38.6 (4.0)
5A	4.6	45			
6	5.4	60	29.4 (9.9)	28.5 (7.1)	36.2 (4.9)
10	10.0	>120	30.5 (9.8)	30.8 (6.8)	43.5 (4.5)
11	15.8		31.5 (9.7)	37.3 (6.9)	46.6 (4.6)
Comm. sample[a]	5.0	40	30.8 (9.4)	31.5 (7.1)	35.6 (4.5)
Comm. sample[b]	10.0	>120	37.3 (8.7)	39.2 (6.3)	40.7 (4.9)

[a]Coco amine.
[b]Tallow propylenediamine.

greater than 30 C. After the addition of 2-2.5 moles of ethylene oxide, as determined by weight loss of the cylinder, the reaction mixture was cooled to 90 C. Addition of ethylene oxide was continued at ca. 25 psi until the desired weight loss of the cylinder was reached. For a typical charge of 250 g of amine the rate of pick-up of ethylene oxide was 125 g/hr after the formation of the 3 mole adduct. At the end of the reaction the autoclave was evacuated using a water aspirator and the volatiles were removed from the product by stirring for 5-10 min under reduced pressure.

Propoxylation. Propoxylation reactions were carried out at atmospheric pressure in laboratory glassware similar to that described above for ethoxylation, except that the calculated quantity of propylene oxide was added to the reaction mixture from a dropping funnel. Propoxylation reactions were also run at ca. 40 psi in the autoclave described above. The preferred temperature range was 180-200 C for the entire reaction. A typical charge of 250 g of amine reacted at atmospheric pressure consumed ca. 50 g/hr of propylene oxide, while the same charge at 40 psi consumed ca. 250 g/hr of propylene oxide.

Analysis and test procedures. Analytical procedures for total and tertiary amine values were based on AOCS Methods Tf-1A-64 and Tf-2A-64 and ASTM D2073-66 with necessary modifications. The total amine values were determined by titration with perchloric acid in glacial acetic acid. Tertiary amine values were determined by prereacting the sample with acetic anhydride followed by a similar titration with perchloric acid. Hydroxyl numbers were determined by a standard acetic anhydride in pyridine procedure. The procedure used was a modification of ASTM D1638-61T in which the volume ratio of acetic anhydride to pyridine was 4:6.

Surfactant properties were determined by the following procedures: surface tension by ASTM D-1331-56, cloud point by ASTM D-2054-65, refractive index by ASTM D-1747-62, pH by ASTM D-1172-56, and wetting by AATCC-17-1952.

Density was determined by weighing an air-free 100 ml sample contained in a 100 ml graduate. Foaming was determined by agitating 200 ml of 0.05% aqueous solution in a Waring blendor for 2 min and noting liquid-foam levels at 0, 2 and 5 min after agitation.

Results of Alkoxylation Reactions

Ethoxylation reactions are summarized in Table I, and propoxylation reactions in Table II. The reaction conditions and the analytical information that was obtained are shown. Molecular weights were calculated from amine values rather than hydroxyl values, since no attempt was made to isolate and analyze the glycol-type impurities in the products.

The ethoxylates prepared in the uncatalyzed reactions were clear, fluid, amber liquids. Their physical and surfactant properties are described in more detail below. To

prepare ethoxylates with a higher than 20 mole ratio, a small amount of NaOH catalyst was added during the latter part of the ethoxylation reaction. In this manner, a 49 mole ethoxylate was obtained as a soft waxy solid.

The propoxylates prepared with catalyst were generally hazy liquids which were clarified by filtering. The white precipitate obtained was a mixture of sodium hydroxide and sodium chloride. The presence of chloride ion was established by precipitation with silver nitrate. The propoxylates were amber liquids that were generally more viscous than the ethoxylates. They were insoluble in water, but soluble in alcohol. The highest mole ratio derivative prepared contained 43 moles propylene oxide and was liquid. Some of the propoxylates were "capped" by adding a weighed amount of ethylene oxide to the propoxylate reaction mixture before the stripping step. The uptake of ethylene oxide was rapid. After the reaction was completed the entire mixture was stripped. The products obtained were analyzed by the analytical procedures described above. The total amine and hydroxyl numbers found were close to calculated values.

Discussion of Alkoxylation Reactions

The reaction patterns found in the ethoxylation of mixed N-alkylethylenediamines are similar to those described by Sanders et al. (8) for the ethoxylation of fatty amines. The polyethoxylation of the mixed N-alkylethylenediamines in the absence of added catalyst proceeds faster at lower temperatures than at higher temperatures while the induction period (the time required for a mole of the substituted diamine to react with 3 moles ethylene oxide) is longer at lower temperatures. From these facts the overall reaction period for a given ethylene oxide adduct may be minimized by adjusting the reaction temperature during the induction and polyethoxylation periods. As the addition of ethylene oxide proceeds after formation of the 3 mole adduct, the self-generated quaternary ammonium compound decomposes or diminishes in concentration, and the reaction slows down to such a point that a catalyst addition and increased temperature are necessary to continue ethoxylation. This point, however, is not reached until 20 moles of ethylene oxide is reacted per mole of

TABLE V

Foaming and Stability of Ethoxylates

Run no.	Mole ratio, EO/amine	pH	mm Foam, min	
			0	5
7	7.4	9.4	72	25
		7.1	75	27
		3.8	80	17
15	17.8	9.1	83	6
		6.5	87	32
		4.2	83	24
17	21.2	9.3	75	4
		7.5	80	4

TABLE VI

One-Shot Rigid Urethane Foams

Materials	Type of amine polyol			
	Witcamine ED-14 3 mole ethoxylate	Thanol R-393-N (Jefferson)	Quadrol (Wyandotte)	None
Propoxylated Sorbitol, g 464 OH no	40.0	40.0	20.0	40.0
Amine polyol, g	4.9	3.6	1.5	—
Dabco 33 LV, g	0.3	0.3	0.15	1.0
Surfactant, g Silicone L-5320	1.0	1.0	0.5	1.0
Freon 11, g	16.0	16.0	8.0	16.0
Crude MDI, g	52.6	52.6	26.3	52.6
NCO/OH	1.05	1.05	1.05	1.18
Properties				
Cream time, sec	90	144	125	132
Rise time, sec	330	480	520	400
Density lb./ft^3	1.97	1.99	---	1.96
Compressive strength, psi	19.4	18.3	---	21.8

mixed N-alkylethylenediamines. For these reasons addition of catalyst to the reaction mixture is not necessary if the desired compound is less than a 20 mole adduct.

The propoxylation reaction proceeds differently in comparison to the ethoxylation reaction. During the propoxylation there is no indication of the presence of a self-generated catalyst. Propoxylation beyond the 3 mole adduct requires an alkaline catalyst. The optimum amount of sodium hydroxide catalyst necessary for the propoxylation was determined by the gradual addition of the catalyst during the reaction until a reasonably constant propylene oxide takeup was obtained. The optimum amount necessary for the propoxylation was found to be 2.5-3.0%.

Another difference between ethoxylation and propoxylation becomes evident on examination of the tertiary amine values obtained for the products. As noted in Table I the tertiary amine content of a 3 mole ethylene oxide adduct is above 90% and is essentially 100% at about a 5 mole adduct ratio. The propylene oxide adducts as noted in Table II contain ca. 80% tertiary amine at the 3 mole level and approach 100% tertiary amine above the 40 mole ratio level. We believe this later phenomenon is due to the steric factors inherent in adding the propylene oxide molecule to the isopropanolamino group.

The materials balance on ethoxylation of mixed N-alkylethylenediamines showed a loss of ca. 10% of the ethylene oxide added during the reaction to form the 17 mole adduct. This loss was probably caused by the nitrogen gas sparging through the system. As expected, the materials balance on the same reaction run under pressure did not show any measurable loss of reactants.

Properties of Ethoxylated Mixed N-alkylethylenediamines

Table III shows the physical properties of a range of ethoxylates, containing from 3-21 moles of ethylene oxide. The refractive index, density and cloud point responses to increasing ethylene oxide ratios are predictable and similar to those of typical of nonionic ethoxylates. At least 3 moles ethylene oxide per mole of mixed N-alkylethylenediamines is necessary to confer water solubility at room temperature, and up to ca. 10 moles of ethylene oxide ensure water solubility up to the boiling point. The cloud points decreased in the expected manner with increasing amounts of sodium chloride as an electrolyte.

Table IV shows the surface acitivity of a series of ethoxylated amines containing 3-15 moles ethylene oxide. Surface activity, as shown by surface tension and Draves Wetting values showed a maximum activity at ca. 4 moles ethylene oxide. Surface acitivity decreased gradually with

increasing ethylene oxide ratio as shown by increasing surface tension and wetting values. Slight loss in surface activity was also noted in acidic solutions of these ethoxylates.

Limited foaming experiments conducted on the aqueous solutions of the ethoxylates, using high rates of shear at temperatures below their cloud points, showed slight response to both mole ratio and pH change initially; while rate of foam decay, exemplified by 5 min readings, showed a moderate response to pH and mole ratio change. These values are noted in Table V.

The physical and surfactant properties of the ethoxylates are closely comparable with the ethoxylate derivatives of coco amine and coco and tallow propylenediamines. The latter are commercial materials used in fiber and textile treatment applications. Screening tests by a textile manufacturer indicated that the ethoxylates of the mixed N-alkylethylenediamines will perform similarly.

Urethane Foams from Propoxylated Mixed N-alkylethylenediamines

Since the propoxylates are less likely to be useful in surfactant applications, several preliminary trials were made with both propoxylates and ethoxylates in urethane foam formulations. In general the ethoxylates reacted much too rapidly with isocyanates in the absence of catalysts, and no useful foams were obtained. The propoxylates were a little slower to react but were not suitable as the total polyol ingredient. Since dilution with standard commercial polyol was indicated, several hand-mixed, rigid foams were prepared in paper containers, the composition and properties of which are shown in Table VI. The results show that the fast reactivity of the described alkoxylates offers possibilities for use in practical urethane systems.

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