Refractive Index of Alcohol Nonionics

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Abstract

Refractive index is a rapid and consistent method of analysis for alcohols and nonionics from normal alcohols and ethylene oxide. Correlations of refractive index with hydroxyl number of alcohols and nonionics are excellent and measurement error is considerably lower for refractive index. Refractive index affords a measurement of the amount of ethylene oxide in nonionics and can be used as a replacement for the 1% cloud point analysis. The ethylene oxide adduct distribution has no effect on refractive index. Specific adducts, a narrow range of adducts made by acid catalyzed ethoxylation and a broad range of adducts made by base catalyzed ethoxylation give the same refractive index value for any given ethylene oxide content.

Applications for the refractive index method for the laboratory and plant are: alcohol blending control, calculation of ethylene oxide requirements for ethoxylation, nonionic control analysis, calculations of hydroxyl number for sulfations. Also, refractive index can help identify laboratory samples, indicate the 1% cloud point and predict the phase character of nonionics.

Introduction

In the detergent field rapid and consistent methods for analyzing alcohols and nonionics are needed. Hydroxyl number analyses of both alcohols and nonionics and the per cent ethylene oxide in nonionics are important to the industry. Several methods for determining hydroxyl numbers of alcohols and nonionics by chemical hydroxyl analyses have been developed and cited in the literature.[1-6] These methods are time-consuming and frequently are not accurate enough for the specifications desired. The per cent ethylene oxide in nonionics is measured by the 1% cloud point analysis. The method is consistent but can be time-consuming and is limited to narrow ranges of ethylene oxide.

Ethoxylation of primary straight chain alcohols and sulfation of nonionics in our laboratories require large numbers of analyses. Waiting for these hydroxyl values often delayed subsequent work.

Refractive index appeared to be the answer for a rapid and consistent analysis for alcohol and nonionic samples. Data were collected to examine correlations of refractive index with hydroxyl number of alcohols and nonionics and per cent ethylene oxide in nonionics.

Experimental

Ethoxylation

Nonionics used in this study were made from a base-catalyzed ethoxylation of primary straight chain alcohols. The ethoxylations were carried out in an autoclave at 160–180C. The ethylene oxide addition was controlled by pressure demand through a research control valve with a Foxboro Controller set at the desired reaction pressure. The amount of ethylene oxide added was measured by the weight loss in the ethylene oxide cylinder suspended on a Baldwin strain cell. The digital read-out on the Baldwin strain cell gave readings to the nearest 2/1000 of a pound. When the desired amount of ethylene oxide had been added the products were post-stirred until essentially all the ethylene oxide reacted. This was determined by a drop in pressure to a constant level. The ethylene oxide content of the nonionics was controlled by this manner to within ±0.1%.

Refractive Index Measurement

Refractive indices were measured on a Bausch & Lomb precision refractometer which can be read to the fifth decimal (5-place) and a Bausch & Lomb refractometer which can be read to the fourth decimal (4-place) using a D light of a sodium arc. A constant temperature bath controlled the temperature at 41C ± 0.1C. The sample was heated to 40–41C, placed on the prism and allowed to reach temperature equilibrium with the prism. Temperature equilibrium was reached in 1 to 2 min. With the 5-place refractometer, after temperature equilibrium had been reached, no change by one operator was observed in consecutive 10-second readings. This gave a repeatibility error with the 5-place refractometer of essentially zero. The repeatability error of the 4-place instrument was larger than zero because of the need to estimate the 4th place without the use of a Vernier scale.

Discussion

Comparison of Errors—Alcohol Hydroxyl Number vs. Refractive Index

Hydroxyl number determinations were made on 49 samples of alcohols in the range of C_{12} to C_{13} by duplicate and triplicate chemical hydroxyl analyses (1). Refractive indices of the alcohols were obtained by the 5-place refractometer at 41C. The data was plotted refractive index at 41C vs. hydroxyl number of the alcohols (Fig. 1). This gave a hydroxyl range of alcohols from approximately 272 to 308 and a refractive index range of 1.43430 to 1.43830.

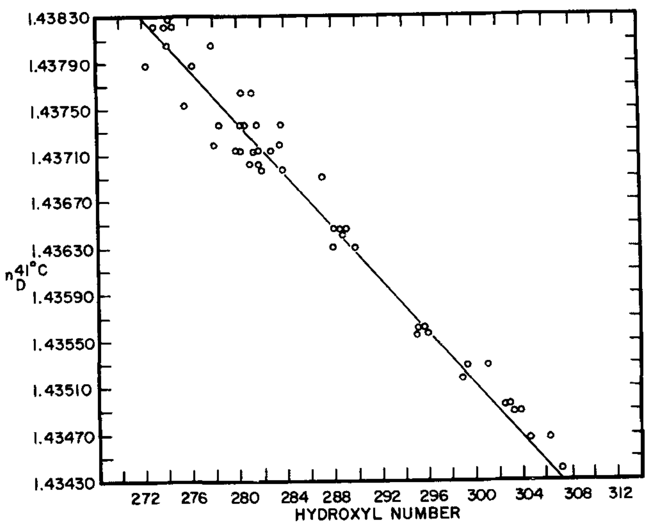

FIG. 1. $n_D^{41°C}$ vs. hydroxyl number of alcohol blends.

TABLE I
Refractive Index Measurements

	5-place Refractometer			4-place Refractometer				
Date operator	6/5/64 A	6/8/64 B	6/8/64 A	6/9/64 B	6/9/64 C	6/9/64 D	6/9/64 E	6/9/64 F
Nonionic A	1.44331	1.44331	1.44314	1.4433	1.4433	....	1.4435	1.4432
B	1.44325	1.44320	1.44325	1.4435	1.4435	1.4435	1.4433	1.4432
C	1.44364	1.44359	1.44336	1.4435	1.4435	1.4434	1.4434	1.4436
D	1.44331	1.44325	1.44325	1.4432	1.4432	1.4432	....	....
E	1.44348	1.44342	1.44331	1.4434	1.4434	1.4434	1.4435	1.4432
F	1.44304	1.44304	1.44314	1.4431	1.4431	1.4431	....	....
G	1.44325	1.44325	1.44331	1.4432	1.4432	1.4434	1.4433	1.4432

σ^2 (variance) on 5-place readings = 46×10^{-10}
σ^2 (variance) on 4-place readings = 86×10^{-6}

The curve shown is the least squares curve describing the data points. It shows a linear relationship within the alcohol range observed. An analysis of error was obtained by calculating the repeatability error of the triplicate hydroxyl number analyses and the reproducibility error of the refractive index analyses.

The reproducibility error of refractive index measurements was calculated by independently measuring seven samples of nonionics with the 5-place refractometer. Table I gives the results of the measurements along with measurements made on the 4-place refractometer.

The variance calculated from Table I gives a measure of the reproducibility error of the refractive index readings. This error with the 5-place refractometer represents approximately 14% of the total error found in the correlation of hydroxyl number with refractive index. The repeatability error of the refractive index measurement as previously stated was essentially zero and contributes nothing to the total error.

The repeatability of the triplicate chemical hydroxyl number analyses was calculated by analyzing 10 samples of alcohols by triplicate chemical hydroxyl number analyses. The variance was calculated and it was found that the repeatability error of the triplicate chemical hydroxyl number analyses represents 76% of the total error in the correlation. By difference all other sources of error represent 10% of the total error.

It is obvious from this analysis that the main cause for variance in data points from the correlation line is error in the hydroxyl number analysis. This error relationship should hold for nonionics as well.

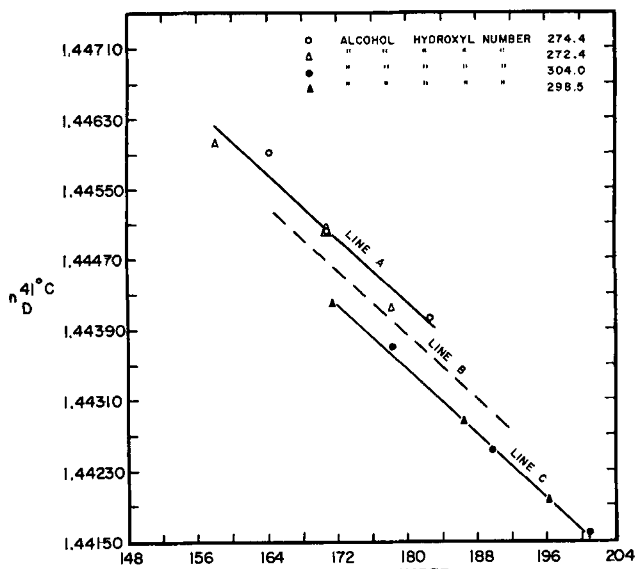

FIG. 2. $n_D^{41°C}$ vs. hydroxyl number of nonionics.

Correlation of Nonionic Hydroxyl Number with Refractive Index

Typical laboratory procedure for sulfation of nonionics has been to calculate the sulfation reagent based on hydroxyl number. It is interesting to compare hydroxyl number with refractive index for limited ranges of ethylene oxide contents on nonionics. Fig. 2 shows data which would represent a range from 35–43% ethylene oxide.

Four alcohol blends were ethoxylated to three levels of ethylene oxide each. The nonionics were analyzed by triplicate chemical hydroxyl number analyses. Refractive indices of the nonionics were measured with the 5-place refractometer at 41C. The average of the hydroxyl number analyses for each nonionic was plotted vs. refractive index of the nonionic (Fig. 2). Two of the alcohol blends consisted of C_{10}, C_{12} and C_{14} alcohols and had hydroxyl numbers of 298.5 and 304.0 calculated from refractive index. The other two alcohols were C_{12} and C_{14} alcohol blends and had hydroxyl numbers of 272.4 and 274.4 calculated from refractive index. Line A in Fig. 2 connects the data points of the nonionics made from the alcohol blends with hydroxyl numbers of 272.4 and 274.4 Line C connects the data points of the other two nonionics.

Line B in Fig. 2 was drawn equidistant from lines A and C and represents nonionics made from alcohols with a hydroxyl number of 287.3.

These data again show that within the alcohol and ethylene oxide content range studied refractive index has a straight line correlation with hydroxyl number. It is obvious that the original alcohol determines the location of the line and that lines for the different alcohol nonionics will be parallel.

For use in sulfation we can see how a series of refractive index curves can expedite analysis. The frequency of curves for the various alcohol raw materials is optional. Reasonable interpolation is justified between alcohols.

Correlation of Per Cent Ethylene Oxide in Nonionics vs. Refractive Index

The straight line relationship between refractive index and ethylene oxide content (measured by hydroxyl number in the preceding section) does not hold beyond 10% ranges of ethylene oxide. Fig. 3 shows a series of curves for nonionics from various alcohols plotting refractive index vs. ethylene oxide content. The refractive index for these products was measured on a 4-place instrument. The products' composition were obtained by careful weight control to within 0.1%.

A number of attempts were made to transform the

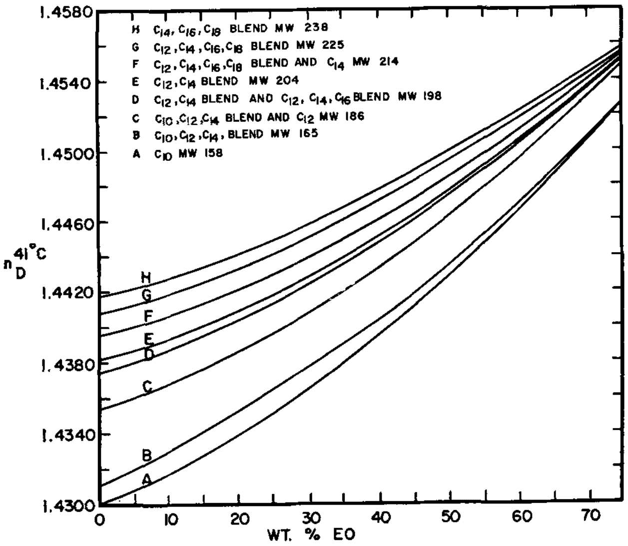

FIG. 3. $n_D^{41°C}$ vs. weight percent EO in nonionics.

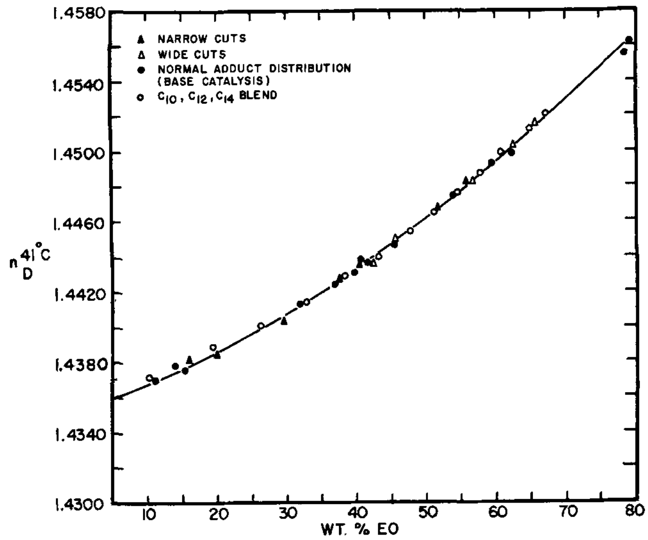

FIG. 4. $n_D^{41°C}$ vs. weight percent 186 MW alcohol nonionics.

refractive index relationship with ethylene oxide content into a straight line. Refractive index vs. moles of ethylene oxide is considerably more curved than vs. weight per cent ethylene oxide. The set of curves in Fig. 3 is nearly straight for 10% increments down to about 35% ethylene oxide. But at the lower ethylene oxide level there is considerable curvature. It is apparent that a transformation to correct for the early curvature might induce curvature in the latter portions. The refractive index of all curves approach that of polyethylene glycol. Since the refractive index of low carbon range alcohols is low and that of polyethylene glycol is high, there is more curvature in those curves than for the nonionics derived from the higher carbon range alcohol.

Different catalysts, for example acid vs. base, will give a different distribution of adducts in nonionics (7). The effect of the distribution of the adducts in a nonionic on refractive index of the nonionic was checked. Samples of C_{12} alcohol were ethoxylated to 40% (2.8 mole) and 62.5% (7.1 mole) ethylene oxide. The nonionics were distilled into cuts. GLC was used to qualitatively determine which adducts were present in each cut. Nuclear magnetic resonance analysis gave quantitative values for the average per cent ethylene oxide in each cut. The cuts from the 40% product contain 2–3 adducts per cut, while the cuts from the 62.5% product contained a minimum of 5 adducts. Refractive indices at 41C were obtained on the cuts with a 4-place refractometer. Refractive indices were also obtained on regular production base-catalyzed C_{12} alcohol nonionics which had not been distilled into cuts and nonionics made from a blend of C_{10}, C_{12}, C_{14} alcohol, with a C_{12} average.

Fig. 4 shows the data from the four sets of products. One curve describes the correlation of refractive index with per cent ethylene oxide in the C_{12} nonionics containing 2–3 adducts, a minimum of 6 adducts, and the wide range of adducts in the regular production nonionics. This shows that the adduct distribution in the nonionic has no effect on refractive index. A specific adduct or narrow range of adducts will give the same refractive index as a broad range of adducts having the same average ethylene oxide content. The fact that the nonionics made from the blend of C_{10}, C_{12} and C_{14} alcohols fit the curve shows that the alcohol distribution in nonionics has no effect on the refractive index. A nonionic made from an individual alcohol gives the same refractive index value as the nonionic with the same ethylene oxide content made from a blend of alcohol with the same average molecular weight as the individual.

The value of this refractive index/ethylene oxide relationship is the simplicity for obtaining control data as well as other data related to the ethylene oxide content. This affords a short cut to obtaining the 1% cloud point, which is also a function of the ethylene oxide content.

Another relationship of interest was observed during this work. The physical state of primary straight chain alcohol nonionics is correlatable to refractive index. The physical state of a large number of nonionics at 78–80F was noted as 1) clear liquid, 2) cloudy two-phase liquid and 3) solid. Refractive indices at 41C were obtained on the samples. It was found that nonionics with a refractive index at 41C below 1.4450 will be clear liquids at 78–80F. Nonionics with refractive index at 41C between 1.4450 and 1.4528 will be cloudy, two-phase liquids at 78–80F. Nonionics with refractive index at 41C above 1.4528 will be solids at 78–80F. The limits are true only for nonionics with a minimum of 20% ethylene oxide. Nonionics containing less than 20% ethylene oxide and alcohols will not fit the correlation.

This information can be used with Fig. 3 to predict the physical state of different nonionics.

Applications

Refractive index measurement is being used as a replacement for the chemical hydroxyl number analyses on alcohols. The method is rapid and gives consistent results. After the standard curves for the alcohols and nonionics are set up, analysis of one sample will take 5–10 min maximum to run. For this application a 5-place refractometer must be used because of the lack of accuracy with the 4-place refractometer.

An example of plant use of the refractive index measurement for the hydroxyl number of alcohols is the ethoxylation of a blend of C_{12} and C_{14} alcohols to a predetermined hydroxyl number of 168. The hydroxyl number of the blend of C_{12} and C_{14} alcohol was found to be 282 using the standard curve of alcohol hydroxyl number vs. refractive index. The amount of ethylene oxide to add to the alcohol has been found by experience to be

$$\text{Lbs EO} = [A \times B/C] - B$$

A = Hydroxyl number of alcohol
B = Lbs of alcohol charged
C = Hydroxyl number of nonionic

This calculation was made and the ethoxylation was run. The finished product was analyzed by duplicate chemical hydroxyl number analyses and found to be 168.

The refractive index method can be used as a control analysis for nonionics and as a replacement for the chemical hydroxyl analyses in calculations for sulfation. When standard curves are set up only the curves representing nonionics made from highest and lowest hydroxyl number alcohols which will be used need to be experimentally determined. The intermediate curves can be drawn from the high and low curves. For example, curve B in Fig. 2 was drawn equidistant from curves A and C and represents nonionics made from alcohols with a hydroxyl number of 287.3. Similarly, other intermediate curves can be drawn.

Conversion of refractive index to hydroxyl number is more accurate for sulfation than the more general correlation with per cent ethylene oxide. Since impurities may be present that do not enter into the ethoxylation reaction, the average ethylene oxide cannot be converted directly to hydroxyl number unless other analytical data are available. Correlations of hydroxyl number with refractive index should be made on the material being processed and thus the impurity contribution is discounted.

The refractive index method can be used to determine the per cent ethylene oxide in experimental nonionics and to anticipate solubility of nonionics by using standard curves as previously shown. This method can also replace the 1% cloud point analysis.

The refractive index method can also be used as a control for alcohol blending. The alcohols are blended by weight, the refractive index of the blend is run and adjustments are made to give consistent alcohol blends.

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