## Nonionic Surfactant Polarity Index Determination by Inverse Gas Chromatography

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ABSTRACT: Polyglycol nonionic surfactants are widely used in industrial and consumer products. Two classes of these surfactants, made from selected combinations of 1,2-butylene oxide, propylene oxide and ethylene oxide, were compared to alcohol ethoxylate (AE) and nonyl phenol ethoxylate nonionic surfactants in this study. Polyglycol copolymers consisted of either a polypropylene glycol (PPG) or polybutylene glycol (PBG) central hydrophobe. Ethoxylation of the hydrophobes produced polyethylene glycol hydrophilic blocks. Differences in hydrophobe polarity were determined by inverse gas chromatography (IGC). IGC is a useful analytical method by which the physical and chemical characteristics of a material are studied. The stationary surfactant material under study was coated onto an inert support and used as the packing for the column. A probe mixture, containing simple organic molecules of varying polarity, was injected, and the retention characteristics were measured. The retention characteristics of the standard probe mixture were used to reveal relative polarity information about the stationary surfactant coatings. Polarities of the four hydrophobes were (in decreasing order): PPG, PBG, nonyl phenyl and fatty alkyl. Comparisons were then made between the calculated hydrophile-lipophile balance values and polarity indices of the hydrophobes and their ethoxylates. The effects of hydroxyl groups on polarity were also studied and quantified. JAOCS 72, 89-95 (1995).

**KEY WORDS:** Alcohol ethoxylate, block copolymer, gas chromatography, HLB, inverse gas chromatography, nonionic surfactant, nonyl phenol ethoxylate, polarity index, polybutylene glycol, polyethylene glycol, polypropylene glycol.

Inverse gas-liquid chromatography (IGC) is a useful analytical method by which the physical and chemical characteristics of materials can be studied. The present work describes a straightforward application of IGC to the problem of determining the relative polarity of a set of nonionic surfactants by using five organic compounds as retention probes: pentane, hexane, heptane, octane and ethanol. The interactions of the hydrocarbons with each stationary phase, which consists of the surfactant material in question coated on a deactivated fire brick support, are similar as evidenced by the retention order. In other words, the retention order of the hydrocarbons coincides with the number of carbons in these molecules. However, the retention order for ethanol relative to the hydrocarbons varies from one stationary phase to the next, which is not surprising because the interaction of ethanol with the stationary phase material is more polar in nature. Hence, it is possible to compute the effective carbon number of ethanol for each stationary phase, with the effective carbon number serving as the basis of a relative polarity index scale for the four surfactant classes under investigation. The IGC technique has been quite useful in providing information on stationary phase coatings, examples of which are hydrophile—lipophile balance (HLB) (1), polymer physical state transitions (2,3) and solubility parameters (4). Another interesting example of the use of IGC is the study of lubricant oxidation (5).

Four classes of nonionic surfactants were studied by IGC: butylene oxide/ethylene oxide (BO/EO) block copolymers, propylene oxide/ethylene oxide (PO/EO) block copolymers, fatty alcohol ethoxylates (AEs) and nonyl phenol ethoxylates (NPEs). Figure 1 shows the structures of the four classes of materials. For polybutylene glycol/polyethylene glycol (PBG/PEG) copolymers, "A" ranges from 10 to 41 and "B" from 0 to 60. PPG/PEG polymers have A values between 7 and 69 with B values ranging from 0 to 76. The degree of



**FIG. 1.** Structures of block copolymers studied by inverse gas chromatography. PBG, polybutylene glycol; PEG, polyethylene glycol; PPG, polypropylene glycol.

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ethoxylation, "Y" and "X," for nonyl phenol (NP) and fatty alcohol, respectively, ranges from 0 to 20.

The relationship between calculated HLB and polarity index is presented, and conclusions are drawn concerning cautions to be considered when using calculated HLB to describe nonionic surfactants of different hydrophobe types.

Data on the effects of terminal hydroxyl (OH) groups on polarity index are also presented, along with the concept of infinitely long polyglycol polarity. Along this same line, the concept of OH-mediated isopolarity is also discussed.

## **EXPERIMENTAL PROCEDURES**

Surfactants and materials. BO/EO and PO/EO copolymers were made by reacting propylene glycol and KOH with the appropriate amounts of BO or PO, and then with EO. AEs were initiated with a C13–C15 linear fatty alcohol (Exxon Chemical, Houston, TX). NPEs were made from NP (Aldrich, Milwaukee, WI). Both initiators were sequentially ethoxy-

lated in single runs in a pressurized reactor to give nominal EO weight percentages of 0, 10, 30, 50, 70 and 80. KOH was used as the polymerization catalyst.

PBG diols of approximately 760, 1060, 1880 and 3000 molecular weight, polypropylene glycol (PPG) diols of 425, 1200, 2000 and 4000 molecular weight, and PEG 1450 were all obtained from The Dow Chemical Company (Freeport, TX). PLURONIC polyol PO/EO copolymers L-61, L-62, L-64 and F-68 were kindly obtained from the BASF Corporation (Parsippany, NJ).

The nomenclature used for the BO/EO and PO/EO copolymers is straightforward. For example, B1050–3.3 indicates a BO/EO tri-block copolymer with a hydrophobe molecular weight of 1050 and an average total degree of ethoxylation of 3.3. Name suffixes for AE and NPE materials likewise describe the degree of ethoxylation. Table 1 summarizes the properties of materials studied by IGC.

Chromasorb P, 60/80 mesh, was purchased from Alltech Corporation (Deerfield, IL). The material came as acid-

Table 1			
Data Describing the Polarit	y of Inverse Gas–Liqui	id Chromatography	Liquid Phases <sup>a</sup>

		Calculated		Ethanol	Polarity
Compound	wt% EO	HLB (%EO/5)	wt% OH	carbon no.	index
B1050–0	0	0.0	3.24	6.25	79.0
B1050-3.3	12.3	2.5	2.85	6.42	83.6
B1050-10.2	30.2	6.0	2,27	6.96	95.4
B1050-20.6	46.5	9.3	1.74	7.29	101.3
B1050-42.1	64.0	12.8	1.17	7.74	108.3
B1050-119	84.1	16.8	0.54	8.49	117.9
B2636-1.4	2.3	0.5	1.26	5.89	67.6
B2166-15.7	24.2	4.8	1.19	6.42	83.6
Pluronic L61	13.4	2.7	1.72	6.86	93.4
Pluronic L62	29.4	5.9	1.40	7.18	99.4
Pluronic L64	38.6	7.7	1.21	7.37	102.7
Pluronic F68	79.3	15.9	0.38	8.71	120.3
Nonyl phenol	0	0.0	7.73	7.59	106.1
NP-0.57	10.3	2.1	6.95	6.91	94.4
NP-2.2	30.6	6.1	5.36	6.54	86.5
NP-4.9	49.7	9.9	3.89	6.89	94.0
NP-10.7	68.2	13.6	2.46	7.59	106.1
NP-20.4	80.3	16.1	1.52	8.11	113.3
C13-15 Alcohol	0	0.0	8.17	5.92	68.6
AE-0.41	8.0	1.6	7.53	5.92	68.6
AE-2.0	29.5	5.9	5.75	6.20	77.6
AE-4.7	49.8	10.0	4.11	6.59	87.6
AE-7.1	60.0	12.0	3.27	6.86	93.4
AE-18.7	79.8	16.0	1.65	7.66	107.1
P-425	0	0.0	8.00	7.48	104.4
P1200	0	0.0	2.83	6.69	89.9
P-2000	0	0.0	1.70	6.58	87.4
P-4000	0	0.0	0.85	6.55	86.7
B746	0	0.0	4.56	6.43	83.8
B764	0	0.0	4.45	6.50	85.5
B-1050	0	0.0	3.24	6.25	79.0
B-1878	0	0.0	1.81	5.89	67.6
B-2957	0	0.0	1.15	5.88	67.2
E-1450	100.0	20.0	2.34	10.07	133.0

<sup>a</sup>EO, ethylene oxide; HLB, hydrophile–lipophile balance; OH, hydroxyl.

washed and silylated. This grade was chosen to ensure minimal interaction of the stationary phase and probes with the solid support. Probe materials were *n*-pentane, *n*-hexane, *n*heptane, *n*-octane and ethyl alcohol (all supplied by Aldrich). Fisher-brand OPTIMA methylene chloride (Fair Lawn, NJ) was used as a carrier for coating the surfactants onto the solid support. A Hewlett-Packard model 5880A gas chromatograph (Palo Alto, CA) was used for all determinations. Peak detection was performed by flame ionization. One-quarter inch o.d. copper tubing was used for the IGC columns. Silanized glass wool (Alltech) was used to secure the packing in the column.

Column preparation and IGC run parameters. Six grams of a neat nonionic surfactant and approximately 100 g methylene chloride was added to a 500-mL fluted flask. To this solution was added 34 g of Chromasorb P to form a slurry. The solvent was slowly removed by rotary evaporation at 25°C. The pressure was decreased gradually during solvent removal, reaching a final pressure of about 10 Torr. The entire solvent removal process took approximately 30 min. The resulting IGC packing was placed into a 90-cm length of copper tubing (described above), one end of which was fitted with connecting hardware and plugged with glass wool. Gradual addition of the packing with gentle tapping on the tubing resulted in a fully packed column. The relatively coarse mesh size of the support simplified the column packing procedure and resulted in sufficient theoretical plates for facile separation of the probe materials.

The remaining end of the packed column was secured with silanized glass wool. It then was fitted with a second set of end-connecting hardware and formed into a 18-cm diameter coil by means of a suitably-sized mandrel. The column was connected to the gas chromatograph, and the oven was set at the conditioning temperature of 80°C with a nitrogen carrier gas flow rate of 20 mL/min. Conditioning was carried out for 12 h. Injection volume was 0.5  $\mu$ L of a probe mixture, consisting of equal parts by weight of *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane and ethyl alcohol. During testing, the set temperatures were as follows: injector, 200°C: oven, 130°C; detector, 150°C. A typical chromatogram is shown in Figure 2. Each surfactant was tested in triplicate, and the retention times for each component were averaged. The variation between determinations was typically less than 0.7% relative SD.

Column temperature is an important factor with regard to interaction of mobile phase components with the stationary phase liquid (6,7). A column temperature of 130°C was chosen to ensure gas–liquid partitioning of the probes, as opposed to interfacial absorption.

The choice of 15% by weight of surfactant on the inert support was the result of a review of pertinent literature (8,9). Also, the injection volume of 0.5  $\mu$ L was small enough to ensure minimal interaction with the inert support. Retention time (t<sub>r</sub>) was used as opposed to corrected retention volumes or retention times (t<sub>r</sub>-t<sub>m</sub>) because of the greater simplicity of the analysis. This was a reasonably good simplification for our purposes due to the negligible effects of the small dead volume and a minimal pressure gradient along the relatively short column.



**FIG. 2.** Representative inverse gas-liquid chromatogram that shows ethyl alcohol elution against *n*-alkane backdrop.

In regard to the sizes of organic probes for the analysis, it has been suggested (10) that polar probes with similar van der Waals volumes may be useful in obtaining a universal polarity scale. Such a correction might be helpful, but was not necessary for this study as our interest was in a relative scale.

## **RESULTS AND DISCUSSION**

Carbon number determination and concepts. As in any gaschromatographic analysis, the retention time of a component is primarily dependent on its interaction with the stationary phase coating. The coating, in our case, was always liquid at an oven temperature of 130°C. The homologous series of probes, consisting of *n*-pentane, *n*-hexane, *n*-heptane and n-octane, were retained, as a group, in proportion to the stationary phase polarity and positioned within this group according to boiling point. Thus, if a fatty alcohol were to be used as the liquid phase, the alkane probes would be retained more strongly (longer t<sub>r</sub>) as a group. If the fatty alcohol were to be ethoxylated to give it higher polarity, the t, would be proportionately lower. Figure 3 illustrates the dependency of tr of the four alkanes as a function weight percent EO for a series of BO/EO copolymers with a PBG hydrophobe of 1050 molecular weight. As the polarity of the surfactant increases (increased EO), the t<sub>r</sub> decreases. Also, the slope for the oc-



**FIG. 3.** Variation of retention time ( $t_r$ ) with wt% ethylene oxide (EO) for *n*-alkanes on ethoxylated polybutylene glycol hydrophobe of 1050 molecular weight. **I**, Pentane;  $\blacklozenge$ , hexane; #, heptane;  $\Box$ , octane.

tane curve is steeper than that of pentane, due to the lower volatility of the octane resulting in more interaction with the liquid phase.

The ethanol component of the probe mixture has a much higher polarity than the *n*-alkanes and functions as the measuring variable for the analysis. A comparison of ethanol and alkane  $t_r$  gives an indication of the stationary phase polarity. As shown in the sample chromatogram (Fig. 2), ethanol is eluted between heptane and octane, thus behaving as a hydrocarbon with a polarity between heptane and octane. Figure 4 shows the relationship between  $t_r$  and carbon number of the *n*-alkanes for the 1050 molecular weight PBG ethoxylate series. The carbon number ranges from five to eight for pentane through octane. By plotting the log of  $t_r$  vs. carbon number for each of the six homologues in the BO/EO series, a separate equation for each material can be determined by linear regression analysis. The equation is of the form:

$$\log(t_r) = A(C\#) + B$$
 [1]

where  $t_r$  is the uncorrected retention time of the alkane, and C# is the number of carbon atoms in the nonpolar probe. A and B are the slope and ordinate intercept, respectively.



**FIG. 4.** Variation of retention time (t<sub>r</sub>) with type of *n*-alkane for 1050 molecular weight PBG hydrophobe ethoxylates. Abbreviations as in Figures 1 and 3.

By entering the  $t_r$  of the ethanol peak, an "apparent" carbon number for ethanol is calculated by using a simple rearrangement of Equation 1. Although the ethanol is not an alkane, the apparent carbon number value obtained by this operation indicates how similarly to an alkane the ethanol interacts with the liquid surfactant phase. Therefore, ethanol will have a variable  $t_r$  against the backdrop of alkanes depending on the relative polarity of the stationary liquid phase. The alkanes are used as an absolute reference system because ethanol  $t_r$  alone do not correspond with stationary phase polarity.

Determination of polarity index. The ultimate purpose of this work was to determine the relationship between ethanol carbon number and surfactant structure. The most obvious place to start data analysis was to plot ethanol carbon number vs. weight percent EO for a homologous series of surfactants with a similar hydrophobe and increasing amounts of EO. In doing so, a nonlinear curve is typically generated. To circumvent this, Heubner (11) determined that, by converting the value to an empirically derived polarity index, a linear function could be obtained. The equation he used was:

$$PI = 100 \log(C\# - 4.7) + 60$$
[2]

where *PI* is the polarity index and *C#* is the apparent carbon number for ethanol. The factor of 4.7 was statistically derived to give the least deviation from linearity. The factor of 100 was chosen so as to convert the polarity index to a whole number, and the term of 60 makes *PI* positive. Table 1 lists the polarity indices of the materials tested.

It must be kept in mind that the polarity scale developed in these experiments with Heubner's approach (11) is a relative one, germane only to the four classes of nonionics studied under our particular experimental conditions.

Inverse gas-chromatographic results on nonyl phenol ethoxylates and fatty alcohol ethoxylates. The plot of log t<sub>r</sub> vs. weight percent EO (Fig. 5) for the AE series of materials was similar in character to that in Figure 3, except for a discontinuity between the C13-C15 fatty alcohol (0% EO) and the first ethoxylated material. This indicates that the alkane probe response to the fatty alcohol hydroxyl group is similar to an alcohol ethoxylated to approximately 30 wt%. However, as will be shown later, the ethanol response presents a better picture of the polarity difference between the initiator and the first ethoxylate. A plot of log t<sub>r</sub> vs. EO% for NPE nonionics was similar to the BO/EO series seen in Figure 3, and there was no sharp discontinuity between 0% EO and the first ethoxylated material as in the AE class. Plots of log t, vs. carbon number for the AE and NPE series were similar to that shown in Figure 4.

Figure 6 shows polarity index vs. wt% EO for the homologous AE and NPE series described above. Notice that, overall, the NPE nonionic is more polar across the entire range of ethoxylation. Interestingly, the NPE curve has a minimum at about 30 wt% EO. This is due to the highly polar (and easily ionized) phenolic hydroxyl group. Below a certain EO percentage, not all of the phenolic OH groups have undergone



**FIG. 5.** Variation of retention time vs. wt% EO for C13–15 fatty alcohol ethoxylates. Abbreviation and key as in Figure 3.

reaction with an EO molecule. The minimum weight percentage of EO needed to react with all phenolic OH groups can be calculated by assuming that 100 g of NP is used as the initiator. This equates to 0.45 moles of NP [molecular weight (MW) = 220] and also to 0.45 moles of OH end groups. Adding the equivalent number of moles of EO would require 20 g of EO feed (MW = 44). This, of course, assumes that each EO monomer added reacts with one NP hydroxyl group and not with an ethoxylated oligomer. This occurs because the phenolic hydroxyl is much more acidic than an ethoxylated phenolic hydroxyl and, thus, more reactive with EO (12). Adding 20 g of EO to 100 g of NP would give a number-averaged MW of 264, corresponding to 16.7 wt% EO. It is at this level of ethoxylation where the true minimum in the curve would probably occur.

For the AE analogs, the polarity is lower compared to the NPEs (Fig. 6). At zero and 8.0% EO, the polarity index is identical. This was alluded to earlier and may be due to the free hydroxyl group of the fatty alcohol being more polar than an AE OH. It is also possible that the higher percentage of



FIG. 6. Effects of increasing wt% EO on the polarity index of fatty alcohol and nonyl phenol ethoxylates (NPE). Abbreviation as in Figure 3.
■, Alcohol ethoxylate; ◆, NPE.

polar hydroxyl groups present in the fatty alcohol lowers the alkane retention times.

Polarity index and its relation to HLB. As discussed above, the HLB of an ethoxylated hydrophobe can be calculated simply by dividing the weight percentage of EO in the molecule by five. At first glance, one might expect the polarity of any two nonionic surfactants of identical HLB values to be the same. However, after analysis by IGC, it was found that this is not true. The nature and polarity of the surfactant hydrophobe must be taken into account, as well as the weight percentage of hydrophilic PEG.

Figure 7 shows a direct comparison of the polarity indices of four classes of nonionic surfactants by plotting the polarity index vs. calculated HLB (%EO/5). The first set is a BO/EO homologous series with a 1050 (nominal) MW hydrophobe. Pluronic PO/EO block copolymers have a hydrophobe MW of approximately 1750. The zero HLB value for the PO/EO series is represented by PPG P-2000. NPEs and linear AEs are also summarized. The BO/EO and PO/EO diols are all triblock copolymers that contain a central PBG or PPG core hydrophobe flanked by PEG blocks. The relative polarity in descending order is PPG, PBG, NP and fatty alcohol. Notice that the curves show a convergence as HLB increases. This is due to a dilution of the hydrophobe component by the PEG moiety.

*Effects of hydroxyl content on polarity index.* The hydroxyl end group contribution to the polarity index is most assuredly an important one, particularly at lower MWs. MW and wt% hydroxyl content are related by the following equation:

$$\%$$
OH = [17(F)/MW] × 100 [3]

where F is the hydroxyl functionality and MW is the numberaveraged molecular weight of the surfactant. The functionality of the BO/EO and PO/EO copolymers in this work is two, and that for NP and AE is one.



**FIG. 7.** Polarity index of four classes of nonionic surfactants vs. calculated hydrophile–lipophile balance (HLB). EO, ethylene oxide; NPE, nonyl phenol ethoxylate,  $\blacksquare$ ; AE, alcohol ethoxylate,  $\blacklozenge$ ; BO/EO copolymer,  $\bigstar$ ; PO/EO copolymer,  $\Box$ .

It was reasonable to assume that a simple PPG or PBG homopolymer would show a measurable decrease in polarity as the MW increased, due to a decrease in the number of polar hydroxyl end groups. It was also reasonable to expect that the baseline polarity index of a PPG of infinite MW (0% hydroxyl) would be somewhat higher than that of PBG, owing to the inherently lower hydrocarbon-like quality of the methyl vs. the ethyl groups along the polymer backbone and the correspondingly higher wt% of oxygen.

As a reference, PEG 1450 was analyzed by IGC to determine the upper limit of the polarity index for ethoxylated hydrophobes. The polarity index for PEG 1450 (Table 1) is 133. However, an infinitely long PEG would have a polarity index slightly lower than 133, due to the disappearance of hydroxyl group effects.

Figure 8 shows the polarity indices of PBG and PPG diols plotted against wt% hydroxyl content. These curves exhibit linearity at lower MW (higher wt% OH) and then tend to show asymptotic behavior when approaching infinite MW (0 wt% OH). Equations for the linear portions of the curves are:

PBG: PI = 6.8(%OH) + 55.8 [4]

PPG: 
$$PI = 2.8(\%OH) + 82.4$$
 [5]

Several important comments can be made based on information from these equations: From Figure 8, the approximate polarity of PPG and PBG diols without hydroxyl contribution (zero limit of hydroxyl) is 86 and 66, respectively. For PBG diols, a change of 1% OH gives an approximate change of 6.8 polarity index units. For PPG diols, a change of 1% OH gives an approximate change of 2.8 polarity index units. This result shows a tendency for PBG polymers to be more sensitive to changes in the OH level than are PPG polymers. This could be explained by the higher overall baseline polarity of the PPG diol hydrophobe compared to PBG diol. The linear portions of both curves in Figure 8 cross at approximately 6.7% OH and a polarity index of 100. The percent OH value at the



**FIG. 8.** Polarity index as a function of wt% hydroxyl content for nonethoxylated polybutylene glycol (PBG) ( $\blacklozenge$ ) and polypropylene glycol (PPG) diols ( $\blacksquare$ ).

intersection corresponds to a diol MW of approximately 510. Near and below this MW, the polarity index is predominantly governed by hydroxyl group percentage and not by polymer composition.

Other work on BO/EO block copolymers with Heubner's approach has been published (13), but there was no mention of hydroxyl group effects, and the range of hydrophobe MWs and EO percentages was narrower than in the present study. However, their conclusions showed that increased EO percentage or decreased MW both led to increased polarity index.

Polarity measurements of broad- and narrow-range AE materials (14) have shown that there are differences between the two types. However, no percent hydroxyl measurements were offered, and effects of hydroxyl level on polarity index were not discussed.

Comparison of nonionics and the concept of isopolarity. To gain additional information on surfactant structure and the effects on overall polarity, materials of essentially identical polarity indices were scrutinized. If two surfactants have the same polarity index, they can be said to be isopolar. The two sets of BO/EO materials exhibiting isopolarity are shown in Table 1. The first set consists of B2166-15.7, B1050-3.3 and B746, each exhibiting a polarity index close to 83.6. In this series of three polyglycols, two effects are acting simultaneously to increase the polarity index. One is the effect of EO content, and the other is hydroxyl group content. However, the two effects act inversely to one another due to the decrease in wt% hydroxyl as ethoxylation proceeds. B746 has more hydroxyl groups than the B2166–15.7 and makes it isopolar, even though it has no EO groups. Table 1 lists some properties of this set of isopolar polymers. Knowing that the three are isopolar, it is reasonable to assume a definable relationship between the two variables of wt% OH and wt% EO at a constant polarity index. Figure 9 shows the linear relationship between these variables. This relation is only valid for BO/EO diols that have polarity indices close to the value of 83.6.

B1878 and B2636–1.4 (Table 1) is another example of isopolar materials, each having a polarity index of 67.6. In this example, B2636–1.4 has approximately 1.4 EO units, with a low wt% hydroxyl content. Figure 9 also shows these two points plotted as percent OH vs. percent EO. Linear equations for the two isopolar curves are:

$$\%$$
OH = -0.14(%EO) + 4.6 (PI = 83.6) [6]

$$\%$$
OH =  $-0.19(\%$ EO) + 1.7 (PI = 67.6) [7]

From the equations of these lines, one can determine that an approximate 0.17 unit decrease (average) in percent hydroxyl is equivalent to an increase in 1.0 wt% EO for BO/EO copolymers of equal polarity index. Moreover, if the family of lines are in fact parallel, and therefore have equal slopes, this generalization would apply to all BO/EO block copolymer diols with this block structure. From these limited data, one can envision a family of isopolar lines that relate wt% OH and wt% EO, each having a Y intercept percent OH value of the corre-



**FIG. 9.** Variation of wt% hydroxyl and wt% EO for two sets of isopolar PBG/PEG copolymers. Abbreviations as in Figures 3 and 8. Polarity index of 83.6, straight line; polarity index of 67.4, dotted line.

sponding PBG diol. To obtain a mathematical expression that relate the three variables of polarity index, percent OH and percent EO, one would need to generate considerably more data to better define the family of lines.

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