temperature, whereas the reference data of commercial resins needed a press time of 3.5 min or longer to have comparable board qualities (Chen, 1981c).

For the conclusion, the results of research indicate the following. (1) Copolymer resins with up to 60% by weight of their standard phenol replaced by the extracts of peanut hulls and pecan nut pith are durable as measured by standard glued wood products tests and these copolymer resins also appear to cure faster and develop durability with shorter press times. (2) The reproducibility of bond qualities is good. Four U.S. patents (Chen, 1980a,b,c,d) and several foreign patents have been issued, based on the research.

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Cloud Point and Phenol Index of Nonionic Surfactants

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The "phenol index" is an excellent parameter to characterize nonionic surfactants. It is useful to determine the effects of additives, to determine an "effective HLB value", and to evaluate the validity of cloud points measured on the same systems. The "effective HLB (hydrophile-lipophile balance) value" indicates an HLB numerically equivalent to the HLB of a reference surfactant, devoid of additives, having the same physical parameters as the surfactant system under investigation. The value of the phenol index is derived from the amount of phenol required to lower a cloud point to the temperature of measurement, 25 °C. We report here a comparison of the phenol index with cloud points and the effect of surfactant molecular weight, surfactant concentration, and intentional additives on the phenol index value.

Introduction
The HLB (hydrophile-lipophile balance) value is a hypothetical value assigned to a given surfactant regardless of the variability of the experimental conditions. The term "effective HLB" (31) refers to an HLB equivalent to the HLB of a reference surfactant which exhibits the same physical properties as the one under investigation (the one under investigation being in the presence of additives; the reference surfactant is without additives). Various methods for determining the effective HLB value in the presence of additives have been described elsewhere (38). They include measurements of cloud point (13,28,51,52), phenol index (31,32,34-36,38), emulsion inversion point (29,30), and phase inversion temperature (1,11,14,33,40,43,50,51).

Because of the limitations in the use of the cloud point, we have previously indicated that a phenol titration is a most effective means for the determination of an effective HLB value of nonionic surfactants in the presence of additives. This simple experimental technique is similar in principle to that used by Karabinos (21) in his study of the determination of polyoxyethylene (POE) chain length where the hydrophobic group is known. The volume in cubic centimeters of the added 5% phenolic solution at the end of the titration is called the "phenol index" (31). Linear correlations have been found between the phenol index values and the HLB of several homologous series of nonionic surfactants using the equimolar concentrations (36). In other words, a decrease or increase in the effective HLB value of a nonionic surfactant caused by additives results in a corresponding decrease or increase in the phenol index value. With this paper we present a fuller characterization of the phenol titration index as compared to the measurements of the cloud point.

The room temperature turbidity of a nonionic surfactant solution arises when the limit of micellar solubilization has been exceeded or from the cloud point depression due to
a solubilizate (49). Phenol depresses the cloud point of nonionic surfactants remarkably (18). Weiden and Norton (54) attributed the lowering of the cloud point by phenol to a decrease in the hydrophilic properties of the micelles. However, Livingstone (26) suggested pH as an important factor in the effect of phenols, although Maclay (27) disputes this.

In a given surfactant–solubilizate system the cloud point and the solubilization limit depend not only on the temperature but also on the relative concentrations of the solubilizate and of the surfactant. The complex relations which exist are best understood if cloud point and solubilization limit curves are traced on graphs where temperature is plotted vs. the amount of solubilizate. The resulting phase diagram, where the system consists of a phenol and a nonionic surfactant, has been reported by Donbrow and Azaz (10). They found that the effect of a phenol on the cloud point is inversely related to the hydrophobicity of the particular phenol. Therefore, in accordance with the above, when phenol is progressively added to a solution of a nonionic surfactant, the turbidity at room temperature (25 °C) is not due to the excess of the solubilizate but it is due to an actual cloud point depression. In other words, the turbidimetric measurement of a nonionic surfactant solution at isothermal conditions as a function of added phenol is related to the cloud point phenomenon. Thus, the change from a single isotropic liquid (below the cloud point curve) is brought about by the addition of phenol at room temperature.

In this paper we will make comparisons between the cloud point and phenol index values hoping that further elucidations on the mechanisms involved will be of considerable assistance in the continued development of this method.

**Experimental Section**

**Materials.** Commercial polyoxyethylated nonyl phenols supplied by Rewo and Hoechst AG, Germany and Berol, Sweden, nominally containing 8, 9, 10, 11, 13, 14, 15, 16, 20, 25, and 50 mol of ethylene oxide/mol of surfactant (abbreviated NPE,) were used as received. The average chain lengths of the ethylene oxide adducts and a mean molecular weight were determined from their hydroxyl values. Their HLB values were calculated on the basis of the Griffin formula (16). The polyoxyethylene derivatives are polydisperse, but Becher (6) has predicted that their properties will be close to that of a homogeneous compound having the composition equivalent to the mean, thereby yielding useful and reasonably reproducible data.

Phenol, resorcinol, pyrogallol, urea, and dioxane were reagent grade materials. Polyethylene glycols (PEG) were products of Huls, AG, Germany.

**Methods.** The cloud points were determined as previously described (28). The phenol index values were measured as follows: a 5% aqueous phenol solution was added dropwise to 50 g of a continuously stirred (0.025 M or 2%, unless otherwise indicated) surfactant solution at a constant temperature (25 °C) until a distinct turbidity marked the end point of the titration. The detailed procedure has been described previously (36).

**Results and Discussion**

**The Effect of the Polyoxyethylene Chain Length of the Surfactant.** Figure 1 shows the effect of the polyoxyethylene chain length on the phenol index values. For the homologous series of surfactants considered here the HLB is, of course, indicative of the hydrophilic portions of the surfactant molecule. As will be noted from the shape of two curves in Figure 1, the best correlation between the phenol index and HLB is obtained when the surfactant concentration is expressed in molal concentrations. When the concentration of NPEa is expressed on a weight percentage scale, the phenol index values increase rapidly with increasing HLB over a relatively short interval of ethylene oxide units (to NPEa with HLB = 15.2). The curve then tends toward a limiting value of 16.0 cm² independent of the HLB values. Consequently, with concentration expressed on a weight percentage basis, the method cannot distinguish between HLB’s above 15.0. However, a linear correlation between the phenol index value and HLB is evident when equimolal concentrations are used. The molecular weight data were calculated from the hydroxyl values of the surfactants. Thus, equimolal concentrations will be used as a calibration curve to determine the effective HLB for surfactants of interest, e.g., in the presence of additives.

Figure 2 shows the effect of phenol on the cloud point of 2% (dotted lines) and 0.025 M (full lines) aqueous solutions of NPEa as a function of POE chain length or HLB value. The cloud point increases in value with an increasing number of ethylene oxide units in the nonionic surfactants. However, the temperature of 110 °C constitutes a practical limit for this measurement. The cloud point curves above 110 °C for NPEa become almost independent of the POE chain length (39). However, a comparison of the depression of the cloud point by phenol at a constant temperature, e.g., 25 °C in Figure 2, indicates that the higher HLB surfactant requires more phenol to
drop the cloud point to room temperature. This is also evident from the increase in the phenol index value with the increase in the surfactant HLB in Figure 1.

The phenol concentrations which lower the cloud point to 25 °C increase with the increasing HLB. This is a linear relationship over a wide range of HLB values when equimolal concentrations of the surfactants are used. Note in Figure 4 that the increase in the phenol index value depends upon the POE chain length. This dependence is also reflected in Figure 3 wherein an increased concentration of phenol is required to give 25 °C cloud points as the HLB of NPE is higher and when concentration of the surfactant shifts from 2 to 6%.

**The Effect of Concentration of the Surfactant.** Figure 4 shows the dependence of the phenol index value on the concentration of the surfactant. The phenol index values rise almost linearly with a corresponding increase in the surfactant concentration.

Figure 3 shows the effect of phenol on the cloud point of 25 °C aqueous solutions of NPE. The cloud point is practically independent of the surfactant concentration between the limits studied here of the concentration for the NPE type surfactants as previously indicated in studies of several authors. However, in the presence of the additive phenol, the cloud point changes wherein the cloud point change depends strongly on the surfactant concentration. As the surfactant concentration increases from 2 to 6%, the effect of phenol is markedly reduced. In other words, regardless of the HLB of the surfactants, the concentration of phenol required to lower the cloud point to 25 °C increases as the surfactant concentration increases. Thus, a comparison of the effective HLB value of different surfactants under the influence of additives should only be made when equimolecular concentrations of the surfactants are used. Note in Figure 4 that the increase in the phenol index value depends upon the POE chain length. This dependence is also reflected in Figure 3 wherein an increased concentration of phenol is required to give 25 °C cloud points as the HLB of NPE is higher and when concentration of the surfactant shifts from 2 to 6%.

**The Effect of the Nature of the Phenols.** Donbrow and Azzam have found that the effectiveness of a phenol in lowering the cloud point is inversely related to its hydrophobicity. In other words, the more hydrophilic phenols lower the cloud point less than the hydrophobic ones. Thus, various phenols will yield different phenol index values. Figure 5 shows the effect of three different phenols, phenol, resorcinol, and pyrogallol, on the cloud point of 0.025 M aqueous solutions of NPE. Note that the more hydrophobic phenol is more effective in lowering the cloud point to 25 °C than the other more hydrophilic phenols. Figure 6 compares the phenol index values of aqueous solutions of NPE (0.025 M) using equivalent concentrations (0.55 M) of phenol in the one instance and resorcinol in the other. Phenol index values for the resorcinol are on the order of twice as large as the corresponding values for phenol. Phenol index values for NPE using a 0.55 M solution of pyrogallol lie above 30.0 cm$^3$.

**Relationships between Cloud Point, Phenol Index, HLB, and Micelle Formation.** Micellization of surfactants is by no means a simple process since the aggregation involves several interrelated factors contributing to the
energy of micellization. Therefore, a universal theory of micellization is still far from being developed, although several aspects have been well described in several reviews (12, 25, 41, 42, 47, 53). In this paper we discuss the properties of micelles in the simplest form.

The micellization process is regulated by the balance between two opposite forces: (1) the cohesive forces between the hydrophobic groups which favor micelle formation, and (2) the affinity of hydrophilic groups to water molecules, which aids in keeping nonionic surfactants in solution. Factors which normally affect the balance between hydration and cohesion (or hydrophilic-lipophilic balance) such as the temperature or additives, also would be expected to affect the formation of micelles.

Basically, the phase separation which occurs at the cloud point is the result of a change in the HLB of the nonionic surfactants as affected by temperature. The cloud point is therefore functionally related to the formation of micelles and their structure. This relationship between the cloud point and the micellar properties of nonionic surfactants was studied by Arai (2) and Kuriyama (24). With a decrease in the cloud point the critical micelle concentration (c.m.c.) decreased, and also the micellar weight increased (this increase of the micellar weight is one of the most important factors in the cloud formation and the phase separation). These relationships were found to hold even in the presence of added salts or alcohol.

On the other hand, the effect on the cloud point of an increase in the phenol concentration closely resembles the effect of a reduction of the number of ethylene oxide units in the POE chain of a series of nonionic surfactants containing the same lipophilic group. This suggests that the mechanism may be a reduction in the hydrophilicity of the ethylene oxide chain due to phenol binding. Thus, the addition of phenol to dilute surfactant solutions can have the same effect as an increase in temperature. Phenol also affects the hydrogen bonding of the surfactant with water, thereby reducing the solvation and water solubility of the ethylene oxide units (10). The resulting change of the effective POE chain length would be expected to influence a number of physical properties of the system relating to both its micellar and monomeric state. For example, an apparent loss of POE groups would lead to a fall in c.m.c., even though c.m.c. in nonionic surfactants is more sensitive to the length of the hydrophobic chain.

Use of the phenol index method for comparisons of the effective HLB of different nonionic surfactants having different polyoxyethylene chain lengths or different additives is based upon the assumption that the surfactants exhibit the same behavior if they have the same cloud point (e.g., 25°C). Therefore, the phenol concentration which lowers the cloud point to 25°C (or phenol index value) is actually a measurement of the hydrophilicity of the effective POE chain length (or effective HLB value in an homologous series).

The Effect of Organic Additives. Figure 7 shows the effect of urea and dioxane on the phenol index values of NPE (0.025 M). Figure 8 shows the effect of phenol on the cloud point of aqueous solutions of NPE (0.025 M) in the presence of urea and dioxane (1.0 M). Urea and dioxane raise the phenol index values and the phenol concentrations required to lower the cloud point to 25°C. Such variations are independent of the POE chain length. Also, urea and dioxane raise the cloud point values of NPE (0.025 M) as shown in Figure 9. Therefore, these additives increase the effective HLB values of NPE. The degree of change of the HLB value is estimated by comparing the cloud point and phenol index values of reference surfactants (no additives) with the values measured in the systems with additives. The changes of the HLB values, using the cloud point method and phenol index method, gave HLB changes of approximately equal magnitude (34). Since both measurements are functions
of the hydrophile-lipophile balance, their agreement is not fortuitous. To provide further insight into the effect of these additives on the HLB value of surfactants, a discussion of the effect of additives on the micelle formation is in order.

Additives which affect micellization and thus the balance between hydration and cohesion (or HLB) may be divided into (1) those which penetrate the micelles and change their structure and (2) those which do not change the environment of the micelles. Roser and Kuhn (27) examined the effect of ethylene glycol monooleate (EGMO) on the c.m.c. increases of aqueous NPE solutions of varying molecular weight. This study revealed a positive effect of EGMO on the c.m.c. values. Similar results were obtained by Schick and Gilbert (45) for aqueous solutions of nonionic surfactants with various molecular weights. These studies suggest that EGMO may have a significant impact on the micelle formation of surfactants.

The Effect of Added Polyethylene Glycols. We previously reported the effects of PEG 400, PEG 1000, and PEG 4000 on the cloud points (30,38) and phenol index values (32,38) of NPE. The polyethylene glycols (1000 and 4000) cause a decrease in the effective HLB of surfactants with a smaller number of ethylene oxide units (e.g., 8–10) as indicated by a decrease of cloud point and phenol index values. All PEG's increase the effective HLB (increase in cloud point and phenol index) for surfactants with ethylene oxide units numbering 12–14. The increase is approximately the same regardless of the PEG added. For long chain ethoxylates (above HLB = 15.0), the greatest increase in effective HLB is caused by the addition of the largest molecular weight PEG. This effect is just the reverse of that observed with the lower molecular weight ethylene oxide adducts. A similar relationship for methoxy polyethylene glycols has also been presented (35).

Figure 9 shows the effect of increasing concentrations of phenol on the cloud point of NPE (0.025 M) in the presence of constant amounts of PEG 400 and PEG 4000. For comparison, Figure 11 shows the effect of varying concentrations of PEG 400 and PEG 4000 on the phenol index values of the same NPE (0.025 M).

The phenol concentration required to drop the cloud point to 25 °C depends upon the molecular weight of PEG and the ethylene oxide chain length of the NPE. This is analogous to the changes in the phenol index values and cloud points caused by the glycol additives.

Cloud Point and Phenol Index of Polyethylene Glycols. Molecules such as the PEG's of various molecular weights show some degree of binding to phenol (17,19), but to a much lesser extent than do the surfactants (23). PEG's have an ether function to participate in hydrogen bonding but have no large lipophilic group. However, Kato (22) has shown the presence of a "micelle-like" structure in simple aqueous solutions of a number of glycols. Therefore, when one forms an association complex between an aromatic moiety and a water-soluble PEG molecule, hydrophobic characteristics are enhanced and an increased amount of phenol may be complexed (8). PEG's, similarly to polyoxyethylene nonionic surfactants, display an inverse solubility-temperature relationship in water and have a so-called cloud point. They are
more soluble at a lower temperature than at a higher one. As dehydration takes place it is generally believed that the polymer molecules change from an extended conformation to a tightly coiled conformation. In the case of PEG's the cloud point decreases with increasing molecular weight approaching a limiting value just below 100 °C (9). The cloud point becomes insensitive to molecular weights above 50,000. An interpretation of the inverse solubility relationship of the polyethylene glycols is based on the hydrophilic–hydrophobic balance in the polymer system (4). The ethylene units and ether oxygens that alternate along the polymer chain provide the hydrophobic and hydrophilic character in the case of PEG. Under these circumstances both solvophilic and solvophobic influences are reflected in the heat and entropy of dilution factors for the polymer–solvent system. The temperature dependence is such that the diluent becomes a nonsolvent at a critical temperature.

The phenol index values for various PEG's as a function of their molecular weights are shown in Figure 12. These phenol index values decrease with increasing molecular weight approaching a limiting value for PEG 20,000 of 16.0 cm³. This relationship between the phenol index value and molecular weight of PEG's forms a curve similar to that of cloud point values vs. molecular weight of PEG's.

It is interesting to recall that a plot of the phenol index vs. ethylene oxide moles for NPE, (also 2%) curves in the reverse direction and also toward a limiting value of 16.0 cm³ (Figure 1). As mentioned previously, when the polyoxyethylene portion of a surfactant molecule prevails, these surfactants approach the properties of the PEG's.

Figure 13 shows the effect of phenol on the cloud point of 2% aqueous solutions of several PEG's. The phenol concentrations which lower the cloud point to 25 °C decrease in a nonlinear fashion with increasing molecular weight of the PEG. The curve approaches a limiting concentration value independent of the molecular weight of the PEG analogous to the curve shown in Figure 12. Cloud point measurements at low temperatures were not always satisfactory because the points were scattered. Additionally, as in the case of NPE₉⁰ (Figures 2 and 4) below 25 °C we observed that at this phenol concentration the oily complex separated out of the aqueous phase as a result of the reduced solubility of the phenol and reduced orientation of the hydrated PEG chain (20). From the shape of the cloud point curves for different PEG's in the upper part of Figure 13 it may be seen that phenol is more effective in lowering the cloud point of the higher molecular weight glycols.

Figure 12. Phenol index values of polyethylene glycols of varying molecular weights.

Figure 13. Effect of various concentrations of phenol on the cloud points of polyethylene glycols.

Conclusions

The advantages of the phenol index method of analysis of nonionic surfactants include: (a) good reproducibility, (b) a rapid determination, (c) a reliable determination, and (d) applicability to a wide range of HLB values, e.g., in comparison to the cloud point method. The phenol index method is a useful tool widely applicable to the study of the effective HLB value of surfactants in the presence of additives.

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Smokeless Fuel from Carbonized Sawdust

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Sawdust from five types of wood was carbonized at 600 °C. Carbonization of teak wood sawdust was studied in detail and the temperature required for producing char suitable for use as smokeless domestic fuel was arrived at. The tar, pyroligneous liquor, and gas emanating from carbonization were subjected to thermal cracking on firebrick pieces, before condensation. Effect of temperature of cracking on the yield and quality of gas was studied. Cracking over semicoke/charcoal at 950 °C resulted in almost complete decomposition of tar and pyroligneous liquor into gas of low calorific value. From the enthalpy balance for the cracking process the endothermicity of the process was evaluated. Conceptual schemes for the cracking of tar and pyroligneous liquor are presented.

Introduction

It is estimated that about two million tons of sawdust less than 1 mm in size is produced in India as a byproduct in the timber industry. Though a part of it is used in particle board industry, and some directly as fuel, a major portion still remains unutilized and its disposal is a serious problem faced by the timber mills. Briquetting of sawdust to make logs (Sadakichi, 1969) for use as domestic fuel is not a solution as it leads to atmospheric pollution during combustion. Carbonization of sawdust followed by briquetting of residual char (Stamn and Harris, 1954) to get a smokeless fuel appears to be attractive. The char can also be used for the preparation of activated carbon (Hassler, 1951). In the context of the present energy crisis, production of smokeless fuel for domestic use from waste of a renewable source such as wood deserves serious consideration in a country like India.

The volatile products obtained from the carbonization of sawdust consist of wood tar, pyrolynguine liquor containing acetic acid, methanol, formic acid, etc., and non-condensable gas comprising mainly CO, CO₂, H₂, and CH₄. The composition of pyrolynguine liquor was studied and various methods have been suggested for the recovery of chemicals (Klar, 1925; Piret de Bihain and Padaki, 1978). However, these methods are not economically attractive compared to the synthetic routes unless the processes are carried out on a sufficiently large scale. The pyrolynguine liquor which constitutes a major percentage of the volatile products, is highly acidic (pH 4) and its handling poses corrosion problems. Its disposal through biological oxidation is problematic because of the high biological oxygen demand value. Wood tar, which is the next major component of the volatile products, is also acidic and its use as fuel poses corrosion problems.

To avoid problems involved in profitable utilization of the tar and pyrolynguine liquor, one method that could be adopted is to subject them to cracking before condensation so that a gaseous product of fuel value and negligible amounts of liquid products are obtained. This will be more suitable when the carbonization is done on a small scale. The gas obtained can be used as a fuel in boilers or furnaces. No work appears to have been carried out on the cracking of the volatile products of carbonization of sawdust, before condensation, to get a gas of fuel value. The present paper describes the experiments carried out on carbonization of sawdust followed by the cracking of the resulting vapor and gaseous products before condensation, so that char suitable as smokeless domestic fuel and gas suitable for industrial use are obtained and liquid products are eliminated.

Materials and Methods

Sawdust collected from different types of locally available wood was used in these studies. The apparatus used for the carbonization experiments was similar to that used for low-temperature carbonization assay of coal (Himus, 1954; Campbell, 1951). It comprises of electrically heated tubular furnace (furnace no.1, Figure 1) a fused silica assay tube 300 mm long and 21 mm in diameter with a side tube 25 mm from the end, a U-shaped glass condenser (cooled externally with ice), and an aspirator of 10-L capacity with arrangement to maintain constant pressure. The procedure adopted for the carbonization experiments on sawdust was the same as that prescribed for coal except that: (i) the initial temperature of the furnace was maintained at 100 °C before it was brought onto the assay tube; (ii) the temperature of the furnace was brought to the desired level at the rate of 5 °C/min and then maintained for 1 h; (iii) about 10 g of sample was taken for the experiments instead of 20 g. The temperature of first evolution of gas and the temperature of evolution of the oil vapor were noted. At the end of the experiment the weight of charcoal, the weight of tar and pyrolynguine liquor together collected in the condenser, and the volume of the gas collected in the aspirator, its temperature, and pressure were noted. The mixture of tar and pyrolynguine liquor from the condenser were carefully washed with

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