

## 보조계면활성제의 계면에서의 분자면적과 계면장력 거동

金 天 姬

한남대학교 사범대학 가정교육과

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## Molecular Area and Interfacial Tension Behavior of High Efficiency Cosurfactants

Chunhee Kim

Department of Home Economics Education, Hannam University, Daejeon 300-791, Korea

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**요 약.** Gibbs' adsorption isotherms을 이용하여, 계면에서 보조계면활성제 분자의 분자 면적과 계면장력 거동에 미치는 ethylene oxide(EO)와 propylene oxide(PO)의 영향을 조사하였다. 일반식  $C_4H_9O(EO)_m(PO)_nH$ 를 갖는 alcohol들의 보조계면활성제로서의 특성을 연구하였는데, 이 alcohol들은 일반적으로 사용되는 보조계면활성제에 비해서 분자량이 크며 계면활성 또한 큰 특성을 갖고 있다. EO와 PO의 몰수와 이들이 첨가된 상대적 순서는 물/기름 계면에서 alcohol 분자의 분자면적과 계면장력 특성에 큰 영향을 미치는 것을 알 수 있었으며, 다음의 결론을 얻었다. 1) PO는 EO에 비해서 계면흡착 효율은 낮으나, 계면장력 저하 능력은 더 크다. 2) 분자량은 같으나 구조가 다른 분자들, 즉 EO와 PO의 첨가 순서만 다른 분자들의 경우는, 계면흡착 효율이 큰 (계면에서의 분자면적이 작은) 분자들이 계면장력 저하 능력이 더 크다. 3) 동일한 친유기에 EO나 PO가 많이 첨가될수록, 분자들의 계면에서의 분자면적은 커지나 계면장력 저하능력도 커진다.

**ABSTRACT.** Gibbs' adsorption isotherms are studied to assay the structural effects of ethylene oxide (EO) and propylene oxide (PO) moieties on the molecular area and the interfacial tension behavior of molecules at the interface. Several industrial alcohols and isomerically pure alcohols, which have a general structure of  $C_4H_9O(EO)_m(PO)_nH$ , are examined for their cosurfactant properties. They are high molecular weight alcohols and more surface active than the cosurfactants usually used. Results show that the number and the sequence of EO and PO units significantly affect the molecular areas and the interfacial tension (IFT) behavior of these molecules at the water/oil interface. The following conclusions are drawn from the result: 1) PO is more efficient in lowering the IFT and less effective in adsorption than EO. 2) For molecules having the same molecular weight but different structures, smaller molecules are more efficient in lowering the IFT. 3) When more EO, PO, or both units are added to the same hydrophobe, the molecule become bigger and more efficient in lowering the IFT.

### INTRODUCTION

Low molecular weight alcohols, such as *sec*-butanol and isopentanol, have been often used as cosurfactants in the production of microemulsions because of their relative neutrality of partitioning between the aqueous and oil phases.<sup>1-7</sup> Unfortunately their relatively low surface activity results

in high concentrations in the bulk phases rather than at the droplets interface. In order to build high efficiency cosurfactants, we have explored both the precise addition of ethylene oxide (EO) and propylene oxide (PO), and the random addition of the two to increase the surface activity of *n*-butanol as cosurfactants. The hypothesis is that

PO moieties are in oil phase and EO moieties in aqueous phase. Phase behavior experiments using these alcohols as cosurfactants have been reported elsewhere, and the following results were obtained: (1) reduction of cosurfactant requirements for microemulsion formation, (2) increased solubilization, (3) reduction of the temperature at which liquid crystals and gels were formed, (4) reduction of the temperature sensitivity as the level of PO & EO addition increases.<sup>8,9</sup> These species become more surface active and have significantly increased molecular area ( $\omega$ ) at the water/oil interface.

There is considerable information on molecular areas ( $\omega$ ) and interfacial tensions (IFT) available for surfactants, but scant information for alcohols possibly because of activity coefficient concerns at the solubility limit. Verhoeckx *et al.*<sup>10</sup> obtained  $\omega$ 's from Gibbs' plots in two-phase oil/water microemulsion systems containing SDS, *n*-pentanol, NaCl, cyclohexane, and water. Under conditions that also exist for such water/oil microemulsions, the molar ratio, pentanol/SDS, of 2.4 at the interface was found. In the mixed monolayer, the total adsorption (pentanol+SDS) corresponds to about 25 Å<sup>2</sup>/molecule, whereas for pure SDS and pentanol the saturation adsorption correspond respectively to a 54 Å<sup>2</sup> and 36 Å<sup>2</sup>/molecule. Abbassi<sup>11</sup> similarly obtained  $\omega$ 's for anionic surfactants and alcohols as a function of parameters such as temperature, electrolyte concentration, surfactant hydrophobe structure, alcohol concentration, and interface type as variables. He reported that the limiting areas for alkylbenzene sulfonates were 37~42 Å<sup>2</sup>, branched sulfonates were 35~37 Å<sup>2</sup>, and straight chain sulfonates were 22~24 Å<sup>2</sup>. The limiting areas for *n*-butanol and *sec*-butanol were reported as 24.2 Å<sup>2</sup> and 36.1 Å<sup>2</sup> respectively at 25 °C at the water/air interface. He also extrapolated the data from Hutchinson<sup>12,13</sup> and reported the  $\omega$  for *n*-hexanol as 22.9 Å<sup>2</sup>, *n*-octanol as 21.5 Å<sup>2</sup>, and *n*-decanol as 22.4 Å<sup>2</sup>. Hutchinson<sup>14</sup> measured the surface tension of the solutions containing *n*-octyl alcohol and SDS. The  $\omega$ 's were found to be about 30 Å<sup>2</sup> for *n*-octyl alcohol and 37 Å<sup>2</sup> for SDS. Schott<sup>15</sup> studied the surface-chemical behavior of C<sub>12</sub>(EO)<sub>28</sub> nonionic surfactant molecule adsorbed at

the water/air interface and reported an  $\omega$  of 110 Å<sup>2</sup>. He compared the limiting area of C<sub>12</sub>(EO)<sub>28</sub> molecule with the cross-sectional area of a randomly coiled polyoxyethylene (POE) chain of 28 units in water and concluded that the POE moieties were considerably distorted, interpenetrated, randomly coiled, and approximately spherical, and that the packing density of the monolayer was limited by the cross-section of those coils. Elworthy *et al.*<sup>16</sup> studied a series of nonionic surfactants having general formula of C<sub>16</sub>(EO)<sub>*n*</sub>OH where *n* varied from 6 to 21. The  $\omega$ 's at the water/air interface were found to be 38 (*n*=6), 44 (*n*=7), 53 (*n*=9), 72 (*n*=12), 81 (*n*=15), 120 (*n*=21) Å<sup>2</sup>. They concluded that the EO chains determined the  $\omega$  value as did Schott. Schick<sup>17,18</sup> studied many series of nonionic surfactants and concluded that amphipathic molecules orient at the air/water interface with the hydrophobic groups above the interface and the EO chains forming coils in the aqueous phase. The coils in the outer shell of the micelle have the shape of a truncated cone.

The theoretical foundation of this study is based on the Gibbs' adsorption equation. The surface excess concentration and molecular area at the interface are calculated by use of the Gibbs' equation.<sup>14,19-31</sup> The following form of Gibbs equation can be used for the alcohols at the solubility limit.

$$d\gamma = -RT \Gamma_2 d \ln C_2 \quad (1)$$

where  $d\gamma$  = the change in interfacial tension of the solvent,  $\Gamma_2$  = the surface excess concentration of the solute,  $C_2$  = the molar concentration of the solute,  $R$  = the gas constant, and  $T$  = the absolute temperature.

The surface excess concentration,  $\Gamma_2$ , can be obtained from the slope of  $\gamma$  vs.  $\ln C_2$  plots at constant temperature.

$$\Gamma_2 = - \frac{1}{RT} \left( \frac{\partial \gamma}{\partial \ln C_2} \right)_T \quad (2)$$

The molecular area at the interface ( $\omega$ ), in Å<sup>2</sup>/molecule, is calculated from the relationship:

$$\omega = \frac{10^{16}}{N\Gamma_2} \quad (3)$$

where  $N$ =Avogadro's number, and  $\Gamma_2$  is in moles/cm<sup>2</sup>.

The molecular area at the interface provides information on the degree of packing and the orientation of adsorbed surfactant molecules.

Industrial alcohols (HB series) consist of many different species and, in principle, the Gibbs' equation would require a  $\Gamma_2$  term of each of the species. However, if adsorption of the species at the interface is a collective process wherein the surface composition is the same as the bulk phase composition, then equation (1) is applicable with understanding that  $\Gamma_2$  is surface excess concentration of the average molecule and  $C_2$  is the total concentration of all the species.

In this study, the effect of the structure of alcohols on  $\omega$  and IFT behavior at the water/*n*-octane interface are discussed. Maximum adsorption is attained at the solubility limit for alcohols as it is at the CMC for surfactants, where pseudo-phase separation occurs and activity coefficients become constant. The structure of alcohols was systematically changed by adding EO and PO units in a variety of sequences. Industrial alcohols with both EO's and PO's are also examined.

### EXPERIMENTAL

**Materials.** *n*-Octane, anhydrous (99+ %), was obtained from Aldrich Chemical Company. Water was purified with a Milli-Q Reagent Water System (Millipore Corp., Bedford, WA), and the surface tension of this water was 72.7 dyne/cm measured at 25 °C. NaCl, reagent grade (100%), was obtained from Baker Analyzed. *n*-C<sub>4</sub>OH, *n*-Butanol anhydrous (99+ %) Gold Label, was obtained from Aldrich Chemical Company, and *sec*-C<sub>4</sub>OH, *sec*-butanol certified, was obtained from Fisher Scientific Company. The alcohol 2EH(EO)<sub>3,1</sub>OH, (2-ethyl hexanol (EO)<sub>3,1</sub>OH)C<sub>8</sub>H<sub>17</sub>O(EO)<sub>3,1</sub>H, was obtained from Alkaryl Chemical.

C<sub>4</sub>O(EO)H (EO, C<sub>4</sub>H<sub>9</sub>O(EO)H) and C<sub>4</sub>O(EO)<sub>2</sub>H (EO<sub>2</sub>, C<sub>4</sub>H<sub>9</sub>O(EO)<sub>2</sub>H) were obtained from Aldrich Chemical Company. The following isomerically pure alcohols were synthesized.<sup>8</sup> The purity of these alcohols was assumed to be 100%.

PO	C <sub>4</sub> O(PO)H	C <sub>4</sub> H <sub>9</sub> O(PO)H
POEO	C <sub>4</sub> O(PO)(EO)H	C <sub>4</sub> H <sub>9</sub> O(PO)(EO)H
EOPO	C <sub>4</sub> O(EO)(PO)H	C <sub>4</sub> H <sub>9</sub> O(EO)(PO)H
EOPOEO	C <sub>4</sub> O(EO)(PO)(EO)H	C <sub>4</sub> H <sub>9</sub> O(EO)(PO)(EO)H
EOPOEOPO	C <sub>4</sub> O(EO)(PO)(EO)(PO)H	C <sub>4</sub> H <sub>9</sub> O(EO)(PO)(EO)(PO)H

A series of commercially available alcohols, the HB series, was obtained from Union Carbide. EO's and PO's were added randomly with constraint that all species have equal weights of EO's & PO's and, hence, constant EO/PO mole ratios.

50-HB-55	C <sub>4</sub> H <sub>9</sub> O(EO) <sub>2,2</sub> (PO) <sub>1,7</sub> H
50-HB-100	C <sub>4</sub> H <sub>9</sub> O(EO) <sub>5,1</sub> (PO) <sub>3,9</sub> H
50-HB-260	C <sub>4</sub> H <sub>9</sub> O(EO) <sub>10,2</sub> (PO) <sub>7,7</sub> H
50-HB-5100	C <sub>4</sub> H <sub>9</sub> O(EO) <sub>43,8</sub> (PO) <sub>33,2</sub> H

**Solutions.** Stock solutions were made by dissolving a known amount of species studied into water or 25 g/dL NaCl aqueous solution, and diluted to make series of lower concentration solutions.

The density of the aqueous sample solutions were regarded the same as that of a pure water or 25 g/dL NaCl aqueous solution free of the molecules. The density of *n*-octane is 0.703 and that of air is regarded as zero.<sup>32</sup> The density of 25 g/dL NaCl aqueous solution was measured using a pycnometer and found to be 1.161. Table 1 shows the densities of the HB series of alcohols.<sup>33</sup>

**Tensions.** The IFT's were measured using the spinning drop interfacial tensiometer.<sup>34,35</sup> A drop of less dense phase, embedded in denser phase, is deformed by high speed rotation of a cylindrical glass sample tube around its axis.

A very clean apparatus must be used for good results with low tension systems. **Sample tubes** were cleaned by an ultrasonic cleaner in concentrated HNO<sub>3</sub> and rinsed with above mentioned water, and dried in an oven. For most of the systems,

Table 1. The density values for the HB series of alcohols at 40 °C

	density, g/cc (40 °C)
50-HB-55	0.970
50-HB-100	0.997
50-HB-260	1.021
50-HB-5100	1.046

2 mm internal diameter sample tubes were used, but 4 mm internal diameter tubes were also used for the systems with high IFT's. **Septa, Caps, and o-rings** were boiled in the water and air dried. **Pasteur Capillary Pipets (9" length)** were used to fill the aqueous sample solutions, and **3 cc disposable syringes with # 22 needles** were used to inject the oil droplet.

The speed range was between 6.00 and 9.00 msec/rev being adjusted to attain a ratio of the length to diameter of oil droplet was greater than 3.5 to validate the infinite length approximation. Readings were usually done about once per 30 minutes and oil droplets were considered to be at equilibrium when three consecutive diameter readings agree to within about 0.001 cm.

The apparent droplet diameters were corrected for the magnification introduced by the cylindrical glass tube. For diffuse illumination, the correction factor equals the refractive index of the aqueous solution filling the tube which is 1.333 for the pure water and 1.372 for the 25 g/dL NaCl aqueous solution.<sup>36,37</sup>

The IFT is calculated from the expression:<sup>10,38</sup>

$$\gamma = 1/4 r^2 \Delta \rho \omega^2$$

where  $r$  = radius of the cylindrical part of the droplet (cm),  $\Delta \rho$  = density difference of the phases (g/cc), and  $\omega$  = angular velocity of the droplet and the surrounding phase (radians/sec).

$$\begin{aligned} \gamma &= 1/4 \Delta \rho (2\pi v)^2 \frac{d^3}{2^3 \times n_r^3} \\ &= \frac{\pi^2}{8 \times n_r^3} \Delta \rho v^2 d^3 \\ &= \frac{\pi^2 \times 10^6}{8 \times n_r^3} \frac{\Delta \rho d^3}{P^2} \end{aligned}$$

where  $v$  (cycles/second) =  $\frac{10^3}{P}$

$P$  = the period taken from the counter (milliseconds/revolution),  $d$  = the diameter of the cylindrical part of the droplet (cm),  $n_r$  = the refractive index.

**Activity.** We were concerned about the activity coefficients of high concentration systems. The concentration range of surfactants studied in the

past varied from  $\mu\text{M}$  to  $\text{mM}$ ,<sup>19</sup> however, in the present application, concentrations may approach 1 M and activity coefficients may significantly differ from unity. We tried calculative techniques using three different equations of Margules, van Laar, and Wilson from Vapor-Liquid Equilibrium (VLE)<sup>39</sup> to obtain activity coefficients of *n*-butanol and *sec*-butanol at the solubility limit.

Contrary to Abbassi,<sup>11</sup> the activity coefficient of the aqueous *n*-butanol solution at the solubility limit was calculated to be about 0.993 and that of the aqueous *sec*-butanol solution under the same condition was about 1.005, even though there were some variations depending on the data sets and the equations used. There were no VLE data available for the other alcohols, but the activity coefficients of the other alcohols were also regarded as unity, because the concentrations at the solubility limit were still dilute enough to validate this assumption as was done by Verhoeckx *et al.*<sup>10</sup> for pentanol.

## RESULTS AND DISCUSSION

Fig. 1~7 show  $\gamma$  vs.  $\ln C$  plots for alcohol molecules. The interfacial tensions (IFT's), for different concentrations of alcohols, are measured against *n*-octane at 25 °C in the absence of NaCl. Fig. 9 and 10 show the effect of NaCl on the IFT's and the molecular areas ( $\omega$ 's) of alcohols. Contrary to the plots for surfactants, Fig. 1~10 do not show a discontinuity, since alcohols do not undergo micellar pseudo-phase separation. Table 2 shows the  $\omega$  of molecules at the saturation adsorption which is a solubility limit for alcohols. The purpose of this study is to examine the structural effect of ethylene oxide (EO) and propylene oxide (PO) units on IFT and  $\omega$ .

We adopted Rosen's terminology of 'Effectiveness' and 'Efficiency' as follows: The 'efficiency' of adsorption is the negative logarithm of the surfactant concentration in the bulk phase required to produce a 20 dyne/cm reduction in the IFT of the solvent. The 'effectiveness' of adsorption at the interface can be measured by the surface excess concentration at surface saturation ( $\Gamma_m$ ) and

Table 2. The molecular weight and the molecular area values for alcohols

	Molecular weight	Molecular area ( $\text{\AA}^2/\text{molecule}$ )
$n\text{-C}_4\text{OH}$	74	36
$sec\text{-C}_4\text{OH}$	74	42
$\text{C}_4\text{PO}$	132	70
$\text{C}_4\text{POEO}$	176	61
		60(25 g/dL NaCl)
$\text{C}_4\text{EOPO}$	176	68
		69(25 g/dL NaCl)
$\text{C}_4\text{EOPOEO}$	220	53
$\text{C}_4\text{EOPOEOPO}$	278	75
$\text{C}_4\text{EO}$	118	43
$\text{C}_4(\text{EO})_2$	162	55
$2\text{EH}(\text{EO})_{3,1}$	266.4	86
50-HB-55	270	74
50-HB-100	520	86
50-HB-260	970	129
50-HB-5100	3930	217

$\omega$  is inversely related to  $\Gamma_m$ , since it is the maximum value to which adsorption can attain. Even though reduction of surface or interfacial tension depends directly on the surface excess concentration of the molecules, these two parameters do not necessarily run parallel to each other because of the following reasons: If we consider an interface between two pure liquid phases 'a' and 'b', the interfacial tension,  $\gamma$ , is given by the expression  $\gamma = \gamma_a + \gamma_b - 2\gamma_{ab}$ , where  $\gamma_a$  and  $\gamma_b$  are the surface free energies per unit area of the pure liquids, and  $\gamma_{ab}$  is the  $a$ - $b$  interaction energy per unit area across the interface. It is known that the greater the similarity between 'a' and 'b' in structure or in the nature of their intermolecular forces, the greater the interaction between them (and the greater the value of  $\gamma_{ab}$ ) and the smaller the resulting interfacial tension between the two phases.<sup>19</sup>

Fig. 1 shows that  $n$ -butanol is more efficient in lowering the IFT and more effective in adsorption than  $sec$ -butanol. Since the reduction of IFT depends directly on the molar surface excess concentration, smaller molecules can reduce the IFT more efficiently if they have the same molecular weight.

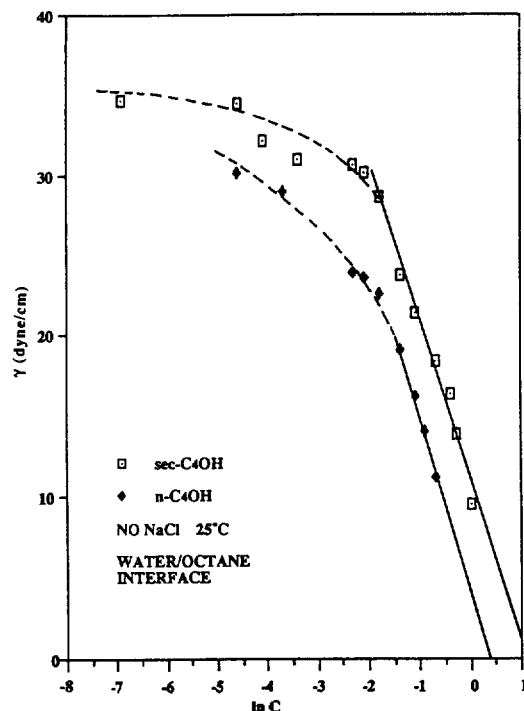


Fig. 1. The  $\gamma$  vs.  $\ln C$  plot for  $n$ -butanol and  $sec$ -butanol at water/octane interface without electrolyte at 25 °C.

The surface excess concentrations, obtained from Gibbs' plots, yield  $\omega$ 's of  $36 \text{ \AA}^2$  for  $n$ -butanol and  $42 \text{ \AA}^2$  for  $sec$ -butanol, with the larger value for  $sec$ -butanol undoubtedly being due to the branched hydrophobe tail. These results are in good agreement with the results by Verhoeckx *et al.*,<sup>10</sup> who reported the  $\omega$  of  $n$ -pentanol at the water/cyclohexane interface to be  $36 \text{ \AA}^2$ . However, these values are bigger than the values that Abbassi<sup>11</sup> reported, which were  $24.1 \text{ \AA}^2$  for  $n$ -butanol and  $36.1 \text{ \AA}^2$  for  $sec$ -butanol at the water/air interface. Since it has long been recognized that cohesion exists between the carbon chains at the water/air interface and that such cohesion is absent at the water/oil interface,<sup>31</sup> these differences might be attributed to the effect of air *vs.* oil for the second phase.

Fig. 2 shows the effect of inserting into  $n$ -butanol either a single EO or PO group. PO is more efficient in lowering the IFT and less effective in adsorption than EO. Because it is well known that

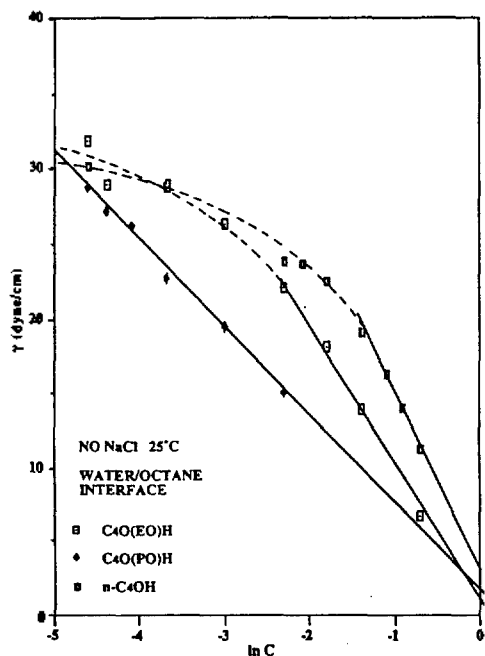


Fig. 2. The  $\gamma$  vs.  $\ln C$  plot for  $C_4O(EO)H$ ,  $C_4O(PO)H$ , and  $n$ -butanol at water/octane interface without electrolyte at 25 °C.

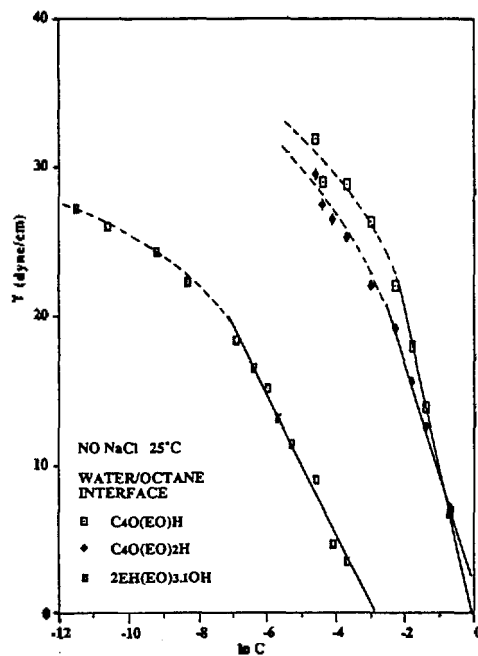


Fig. 3. The  $\gamma$  vs.  $\ln C$  plot for  $C_4O(EO)H$ ,  $C_4O(EO)_2H$ , and  $2EH(EO)_{3.1}OH$  at water/octane interface without electrolyte at 25 °C.

a longer hydrophobe chain is more efficient, it would be reasonable to regard PO as a hydrophobic part and EO as a hydrophilic part. PO molecules form a more expanded film at the interface, resulting in a bigger  $\omega$  than EO molecules, partly because of the bulkiness arising from chain branching. Both EO and PO molecules are less effective than  $n$ -butanol, resulting in a larger  $\omega$ . However, they are more efficient in lowering the IFT. This seemingly contradictory phenomenon can be explained as follows: Added EO or PO units in molecules give a bigger interaction between hydrophilic groups of molecules and water (-EOH and water) or hydrophobic groups and oil ( $C_4PO$ - and oil) than the interaction of  $n$ -butanol with water (-OH and water) or oil ( $C_4-$  and oil). Therefore, EO and PO molecules can reduce the IFT more efficiently, even though they are less effectively adsorbed at the interface than  $n$ -butanol.

Interrelating Fig. 3~5 reveals a number of trends.  $2EH(EO)_{3.1}$  is more efficient than  $EO_2$ , which is more efficient than EO; POEO is more efficient

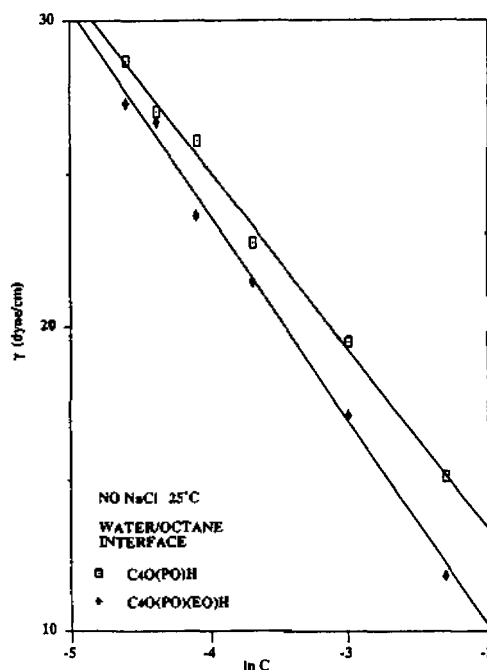


Fig. 4. The  $\gamma$  vs.  $\ln C$  plot for  $C_4O(PO)H$  and  $C_4O(PO)(EO)H$  at water/octane interface without electrolyte at 25 °C.

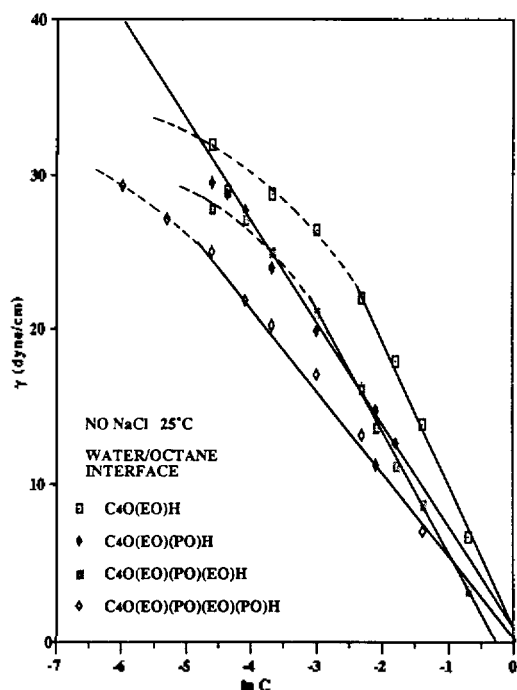


Fig. 5. The  $\gamma$  vs.  $\ln C$  plot for  $C_4O(EO)H$ ,  $C_4O(EO)(PO)H$ ,  $C_4O(EO)(PO)(EO)H$ , and  $C_4O(EO)(PO)(EO)(PO)H$  at water/octane interface without electrolyte at 25 °C.

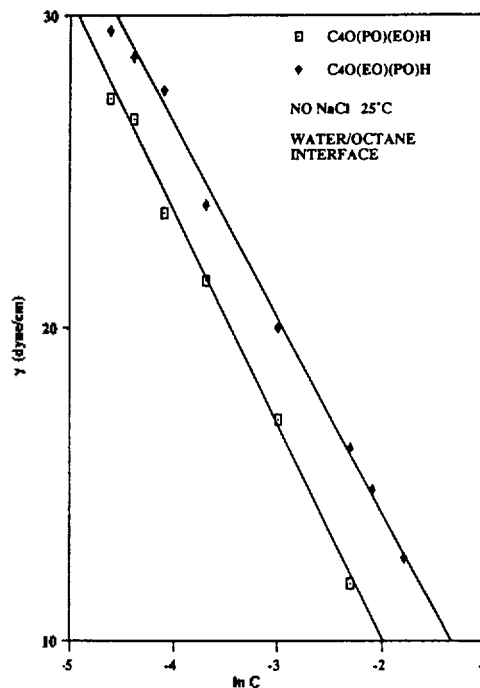


Fig. 6. The  $\gamma$  vs.  $\ln C$  plot for  $C_4O(PO)(EO)H$  and  $C_4O(EO)(PO)H$  at water/octane interface without electrolyte at 25 °C.

than PO; and EOPEOPEO is more efficient than EOPEO, EOPO, and EO. EOPEO and EOPO show similar efficiencies and are more efficient than EO in lowering IFT. From these observation, it can be concluded that the more EO's or PO's added to the same hydrophobe tale, the more efficient the molecule becomes, since EO's and PO's increase the interactions between the molecules and either water or oil phases. The pronounced efficiency of  $2EH(EO)_{3,1}$ , which is in the area between surfactants and cosurfactants, can be explained by Traube's Rule.<sup>14,20</sup> It is, however, impossible to apply Traube's Rule directly, due to both the hydrophobe chain branching and the longer and distributed EO chains of  $2EH(EO)_{3,1}$ . The  $\omega$ 's are obtained from the corresponding slopes of plots and have the following orders:  $EO < (EOPO) < EOPEO < EOPEOPEO$ ,  $EO < EO_2 < 2EH(EO)_{3,1}$ ,  $PEO < PO$ . When EO's and PO's are alternately added,  $\omega$ 's increase, presumably because alternately added EO's and PO's make the molecules lie

flat at the interface due to alternating hydrophilicity between EO's and PO's, except PEO and EOPEO. When PO is compared with PEO and EOPO is compared with EOPEO, the  $\omega$  of PEO is smaller than that of PO and the  $\omega$  of EOPEO is smaller than that of EOPO. This phenomenon can be explained as follows: The last EO units, which is next to an OH, are of enhanced hydrophilicity taken together with the OH group, tends to cause an adjoining PO to be inserted entirely into the aqueous phase.

Fig. 6 shows that POEO is more efficient in lowering the IFT and smaller in  $\omega$  than EOPO. For PEO, PO is next to the hydrophobic chain and EO is attached to the hydrophilic alcohol group, resulting in molecules with greater normal orientation at the interface than EOPO. But the difference (about  $7 \text{ \AA}^2$ ) is not so large, indicating that EOPO and PEO segments of these molecules do not lie flat at the interface but tilt with respect to the interface.

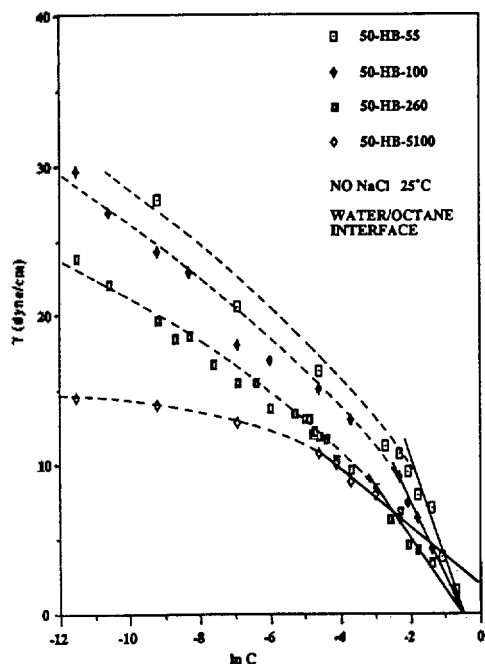


Fig. 7. The  $\gamma$  vs.  $\ln C$  plot for the HB series of alcohols at water/octane interface without electrolyte at 25°C.

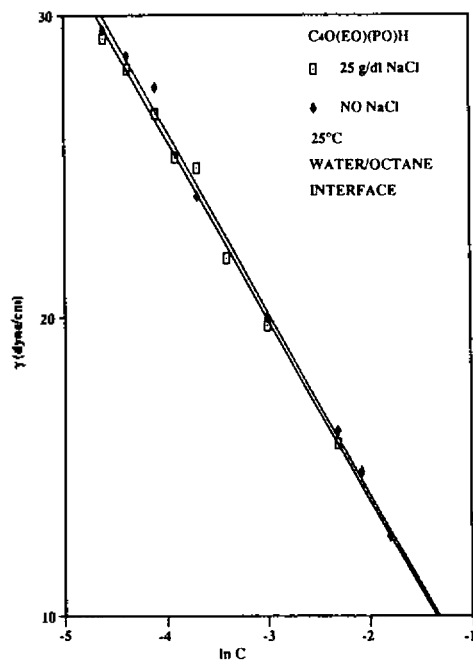


Fig. 9. The  $\gamma$  vs.  $\ln C$  plot for  $C_{12}O(EO)_{20}H$  at water/octane interface with and without electrolyte at 25°C.

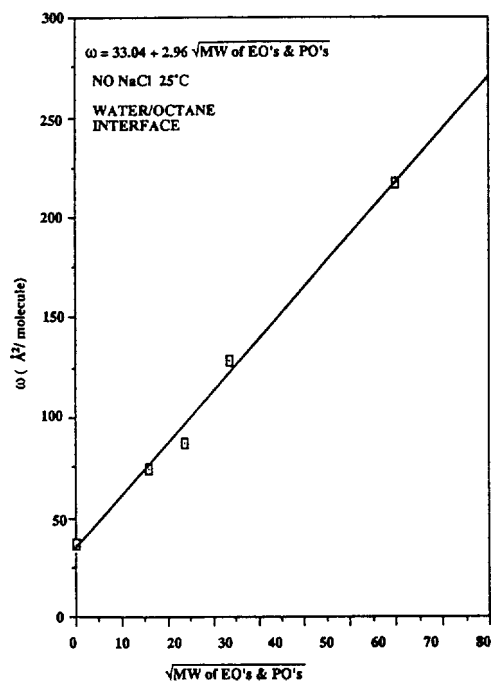


Fig. 8. The  $\omega$  vs.  $\sqrt{MW}$  of EO's & PO's plot for *n*-butanol and the HB series of alcohols.

Fig. 7 shows the plot for the HB series of alcohols. The sequence of EO's and PO's are not known, and the chain length of EO's and PO's have a distribution. The efficiency of adsorption and  $\omega$  increase with molecular weight. The  $\omega$ 's increase with  $\sqrt{\text{molecular weight of EO's \& PO's}}$  and fit the linear equation of  $\omega = 33.04 + 2.96 \sqrt{MW \text{ of EO's \& PO's}}$  (Fig. 8). This equation gives  $\omega = 33.04$  for *n*- $C_4OH$ , which is in reasonable accordance with experimental data of  $\omega = 36$ . 50-HB-5100, which has a total EO and PO number of about 77, has an  $\omega$  of 217 Å<sup>2</sup>. Considering that the  $\omega$  of  $C_{12}O(EO)_{20}H$  has been reported as 110 Å<sup>2</sup>,<sup>15</sup> and that of  $C_{16}O(EO)_{21}H$  as 120 Å<sup>2</sup>,<sup>16</sup> and assuming that the hydrophobe chain length has little effect on  $\omega$ , it can be concluded that PO and EO chains of the HB series of alcohols are randomly coiled at the interface, since EO groups stay in aqueous phase and PO groups in oil phase, the similar way as nonionic surfactants with long EO chains. The  $\omega$  is determined by the cross-section of these coils. However, contrary to the fact that



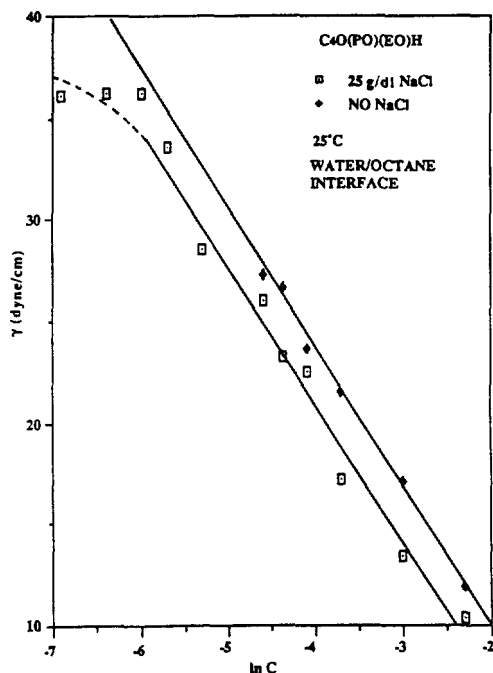


Fig. 10. The  $\gamma$  vs.  $\ln C$  plot for  $C_4O(PO)(EO)H$  at water/octane interface with and without electrolyte at 25°C.

the increase in the EO chain length of nonionic surfactants at the constant hydrophobe chain length results in a decreased surface activity (decreased efficiency),<sup>16,17,20</sup> the efficiency of the HB series increases as EO and PO chain lengths increase, especially at low concentration.

Fig. 9 and 10 show the effect of NaCl on the IFT and on the  $\omega$  of EOPO and POEO molecules. As expected, NaCl has little or no effect on  $\omega$ , at least within experimental error.

### CONCLUSIONS

Gibbs' adsorption isotherms for alcohols were studied to verify the structural effects of ethylene oxide and propylene oxide moieties on the molecular areas ( $\omega$ 's) and the interfacial tension (IFT) behavior. The following conclusions were drawn from the results:

1. Propylene oxide (PO) is more efficient in lowering the IFT than ethylene oxide (EO), consistent with PO functioning as a hydrophobe and EO

functioning as a hydrophile. PO is less effective in adsorption than EO, resulting in a larger  $\omega$  due to chain branching.

2. For molecules having the same molecular weight but different structures, such as *n*-butanol and *sec*-butanol, and  $C_4O(EO)(PO)H$  and  $C_4O(PO)(EO)H$ , smaller molecules are more efficient in lowering the IFT.

3. When more EO, PO, or both units are added to the same hydrophobe, the molecule become bigger and more efficient in lowering the IFT. Because they increase the interactions between the molecules and either water or oil phases, and these effects dominate other effects.

4. For molecules with both EO's and PO's, the sequence of EO's and PO's has significant effects on  $\omega$  and IFT behavior. The molecules with PO units added to hydrophobes and with EO units added to hydrophiles are smaller than the molecules with PO units attached between EO's and hydrophiles.

5. The  $\omega$ 's for the HB series of alcohols increase with  $\sqrt{\text{molecular weight of EO's \& PO's}}$ .

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