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a transfer of 0.2 e$^-$/boron to the conduction band in the metallic structures. The number of itinerant d electrons, important in aligning spins for ferromagnetic metals, is also specified. The formulations lead to approximate valence band DOS which have the same shape as the experimental valence band. These proposed electronic structures which specify the spacial location of d electrons and conduction electrons in interstitial regions account for the gradations in electronic heat capacity, Mössbauer isomer shifts, and for other unique properties of Fe_2B and FeB. The chemical binding in these lower Fe borides is related to that in elemental metals. In FeB there is a degree of covalent binding within the boron chain, but it is considered that the boron chain as well as the individual Fe atoms constitute the positive cores of a metallic lattice with electron density in interstices between Fe and B.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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Relationship of Structure to Properties in Surfactants. 9. Syntheses and Properties of 1,2- and 1,3-Alkanediols

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A number of 1,2- and 1,3-alkanediols containing 10–15 carbon atoms in the alkyl group have been synthesized, purified, and characterized. Surface tension measurements on aqueous solutions of these compounds at 25 °C have been used to calculate surface excess concentration, area/molecule at the aqueous solution/air interface, critical micelle concentration, efficiency and effectiveness of surface tension reduction, and standard free energy of adsorption and of micellization. The compounds appear to be adsorbed at the aqueous solution/air interface in an almost close-packed arrangement with both hydroxyl groups lying in the interface and with the alkyl chain oriented perpendicular to it. The data indicate that, in its surface properties in aqueous solution, a 1,3-alkanediol is very similar to a 1,2-alkanediol with one less carbon atom. The standard free energy of adsorption of the $HOCH_2CHOH-$ or $HOCH_2CH_2CHOH-$ group at the aqueous solution/air interface is 4.3–5.2 kJ mol^{-1}, whereas the standard free energy of micellization of these groups in aqueous solution is 10.3–10.9 kJ mol^{-1}.

Introduction

In spite of the fact that multiple hydroxyl groups appear as a portion of the hydrophilic group in a number of important types of surfactants, e.g., monoglycerides, diethanolamides, and sugar esters, there are almost no data concerning the effect of more than one hydroxyl group on the surface properties of a molecule. This investigation is concerned with the synthesis and properties of some 1,2- and 1,3-alkanediols. Interest in these molecules stems from the use of preparing them from available α-olefins, in the case of the 1,2-alkanediols by direct reaction with hydrogen peroxide[1] (eq 1) and for the 1,3-diols by methanolysis of

$$RCH{=}CH_2 + H_2O_2 \xrightarrow{CH_3COOH} RCHOHCH_2OH \quad (1)$$

the 1,3-dioxanes obtained by the Prins reaction of α-olefins with paraformaldehyde[2] (eq 2 and 3).

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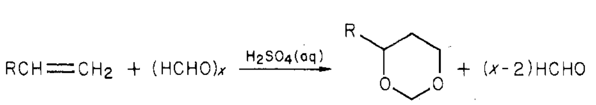

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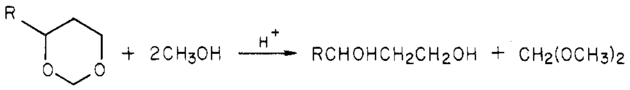

(3)

The products were purified by recrystallization to constant melting point from suitable solvents. Molecular structures of the 1,3-alkanediols (1,3-undecanediol, -tridecanediol, and -pentadecanediol) were confirmed by infrared spectroscopy and elemental analysis.

Surface tension measurements as a function of the log of the concentration of the products in quartz-distilled water at 25 °C were used to calculate surface excess concentrations, area/molecule at the liquid/air interface, critical micelle concentration, efficiency[3] and effectiveness[4] of surface tension reduction, standard free energy of adsorption[5] at the aqueous solution/air interface, and standard free energy of micellization. These measurements were analyzed to show the effect of the two hydroxyl groups on the surface and related properties of the products.

Experimental Section

Synthesis of 1,2-Alkanediols. Decane-1,2-diol and dodecane-1,2-diol were synthesized by the method of Swern.[1] The appropriate 1-alkene (Humphrey Chemical Co., 99% purity) was dissolved in 88% formic acid and treated with 30% hydrogen peroxide for 24 h at 40 °C. After removal of excess formic acid and water by distillation, the residue was refluxed with alcoholic 3 M potassium hydroxide for 1 h and then the excess alcohol removed by distillation. The oily residue was washed with hot water and dried by distillation under reduced pressure in a rotary evaporator, and the residue dissolved in warm petroleum ether. After the solution was cooled, the product was obtained in crystalline form. The product was recrystallized once more from petroleum ether and then from methanol, yielding a material of constant melting point.

The 1,2-decanediol prepared in this fashion had a melting point of 46.8–47.5 °C; the 1,2-dodecanediol had a melting point of 59.7–60.2 °C. The melting points reported by Swern[1] were 48.9 and 60–1 °C, respectively.

The solubilities in water at 25 °C of the 1,2-alkanediols were 0.47 (C_{10}) and 0.032 (C_{12}) g dm^{-3}.

Synthesis of 1,3-Alkanediols.[2] *A. Preparation of 4-Octyl-1,3-dioxane.* To a well-stirred slurry of 45 g (1.5 mol) of paraformaldehyde and 60 mL of 84% (w/w) sulfuric acid maintained at 40–45 °C was added 70 g (0.5 mol) of 1-decene (Humphrey Chemical Co., 99% purity) slowly over a period of 4 h. The mixture was then heated at 55–60 °C for 1.5 h and then at 65 °C until the infrared spectrum of the reaction mixture showed no further increase in the ratio of the ether peak at 1145 cm^{-1} to the unsaturation peak at 1640 cm^{-1} (ca. 3.5 h). The reaction mixture was washed by stirring it vigorously with 100 mL of water at 95 °C for 0.5 h and then twice with 100-mL portions of water at room temperature.

The washed oil layer was distilled at reduced pressure, and the fraction boiling at 104–105 °C at 2–3 torr ($n^{26}{}_{D}$ 1.4426) was collected. The yield of distilled product was 20% of the theoretical. After recrystallization from methanol, the 4-octyl-1,3-dioxane had a constant melting point of 30.0–30.7 °C. The infrared spectrum showed absorption peaks at 1035 and 1145 cm^{-1} due to C–O stretching.

B. Methanolysis of 4-Octyl-1,3-dioxane. A mixture of 6.5 g (0.035 mol) of 4-octyl-1,3-dioxane, 90 mL of methanol, and 0.7 g of concentrated sulfuric acid was heated in a flask with an attached fractionating column to permit the distillation of the dimethoxymethane (bp 45 °C) produced in the reaction. The reaction mixture was neutralized with sodium hydroxide solution; most of the excess methanol was removed by reduced pressure distillation, and the residue was dissolved in 100 mL of water. The aqueous solution was extracted three times with 25-mL portions of *n*-butyl alcohol. Evaporation of the *n*-butyl alcohol extracts yielded the diol.

The 1,3-undecanediol was recrystallized from petroleum ether to a constant melting point of 38.0–38.5 °C. The yield of purified diol was 70% of the theoretical. The infrared spectrum showed absorption peaks at 3250 cm^{-1} due to OH stretching and at 1045 and 1110 cm^{-1} due to C–OH stretching.

The 1,3-tridecanediol, pentadecanediol, and heptadecanediol were prepared from the corresponding 1,3-dioxanes in a similar manner. In these cases, however, the 1,3-dioxane could not be obtained from the reaction mixture by distillation at reduced pressure because of extensive decomposition of the product and was obtained instead by adding hot methanol to the washed, oily reaction mixture and filtering the resulting solution, if necessary, to remove any insoluble material. After the methanolic solution was cooled, the alkyl-1,3-dioxane was obtained as a crystalline precipitate, which was recrystallized twice from methanol and then used to prepare the corresponding 1,3-alkanediol.

The melting points of the 1,3-tridecanediol, -pentadecanediol, and -heptadecanediol were 52.0–52.4, 61.3–61.6, and 70.3–70.8 °C, respectively.

Analytical data for the 1,3-alkanediols were as follows:

	calcd		found	
	C	H	C	H
1,3-undecanediol	70.16	12.85	69.58	12.56
1,3-tridecanediol	72.16	13.04	72.34	12.84
1,3-pentadecanediol	73.71	13.20	73.65	13.00

The solubilities in water at 25 °C of the 1,3-alkanediols were 0.43 (C_{11}), 0.03 (C_{13}), and 0.012 (C_{15}) g dm^{-3}.

Surface Tension Measurements. Solutions of the diols were prepared with quartz-distilled water (specific conductivity 1.1 × 10^{-6} mho cm^{-1} at 25 °C). All surface tension measurements were made by Wilhelmy vertical plate technique, using a sand-blasted platinum plate of ca. 5-cm perimeter calibrated against quartz-distilled water each time measurements were made. The plate was suspended from a dial-type torsion balance capable of being read to 0.2 mg (ca. 0.04 mN m^{-1}). All solutions to be tested were immersed in a constant-temperature bath at the desired temperature ±0.02 °C and aged for at least 0.5 h before measurements were made. Measurements were repeated at 20-min intervals until no significant change occurred.

Results and Discussion

Critical Micelle Concentrations, Maximum Surface Excess Concentrations, and Minimum Surface Areas/Molecule. Plots of the surface tension (γ) of aqueous solutions of the 1,2- and 1,3-diols vs. the log of their bulk phase concentration in mol dm^{-3} (log C) are shown in Figures 1 and 2, respectively.

Critical micelle concentrations (cmc) were taken as the concentrations at the point of intersection of the two linear portions of the γ-log C curve. Surface excess concentrations (Γ), in mol cm^{-2}, and areas/molecule (A), in nm^2, at

TABLE I: Critical Micelle Concentrations (cmc), Maximum Surface Excess Concentrations (Γ_{max}), and Minimum Areas/Molecule (A_{min}) at the Liquid/Air Interface at 25 °C

			A_{min}, nm^2 × 100	
compound	cmc, mol dm^{-3}	Γ_{max}, mol cm^{-2} × 10^{10}	from γ-log C curve	from molecular models[a]
1,2-decanediol	$2.2_6 \times 10^{-3}$	5.1	33	27
1,3-undecanediol	$2.2_9 \times 10^{-3}$	5.3	32	30
1,2-dodecanediol	$1.8_2 \times 10^{-4}$[b]	6.3	26	27
1,3-tridecanediol	$1.4_1 \times 10^{-4}$[b]	5.8	29	30
1,3-pentadecanediol	$1.2_9 \times 10^{-5}$	5.1	33	30
$C_8H_{17}OC_2H_4OH$[c]	4.9×10^{-3}	5.2	32	30

[a] Alkyl chain perpendicular to interface, both hydroxyl groups lying in interface. [b] Below Krafft point; supersaturated solution. [c] K. Shinoda, T. Yamanaka, and K. Kinoshita, *J. Phys. Chem.*, 63, 648 (1959).

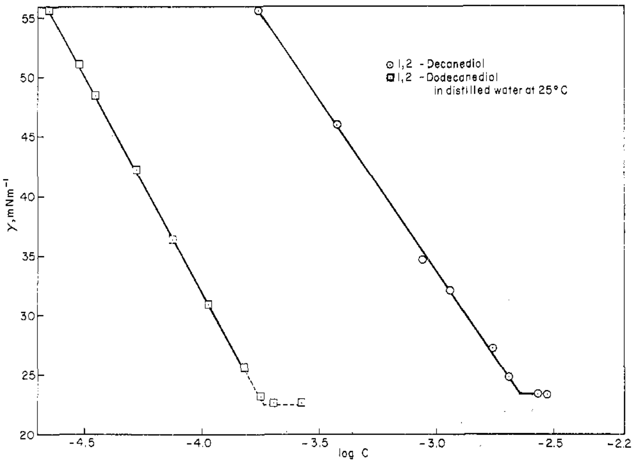

Figure 1. Surface tension vs. log of the concentration of 1,2-alkanediols in aqueous solution at 25 °C.

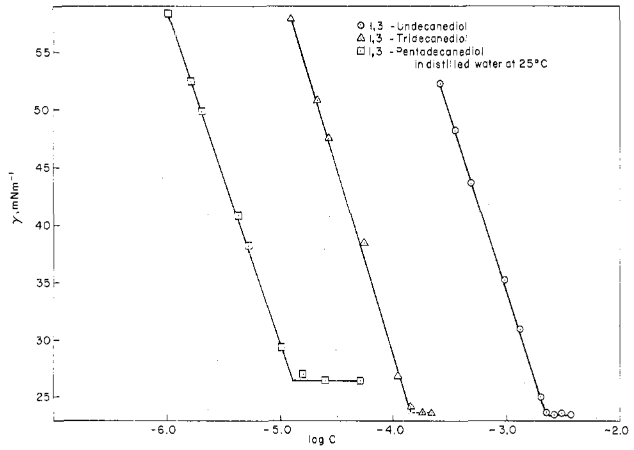

Figure 2. Surface tension vs. log of the concentration of 1,3-alkanediols in aqueous solution at 25 °C.

the liquid/air interface were calculated from the relationships:

$$\Gamma = \frac{1}{2.303RT}\left(\frac{\partial \gamma}{\partial \log C}\right)_T$$

and

$$A = 10^{14}/N\Gamma$$

where $(\partial\gamma/\partial \log C)_T$ is the slope of the γ-log C curve at constant (absolute) temperature, T, R = 8.31 J mol^{-1} K^{-1}, and N = Avogadro's number. Values of cmc, Γ_{max}, and A_{min}, obtained from surface tension measurements, together with cross-sectional areas of the compounds as obtained from molecular models, are listed in Table I. The Γ_{max} values and corresponding minimum surface areas/molecule calculated from the linear portion of the γ-log C curve below the cmc. For comparison, the values for $C_8H_{17}OCH_2CH_2OH$, which is isomeric with 1,2-decanediol, are included.

TABLE II: Surface Tension Reduction Efficiency (pC_{20}) and Effectiveness (π_{cmc}), and cmc/C_{20} Ratios at 25 °C

compound	efficiency, pC_{20}	effectiveness (π_{cmc}), mN m^{-1}	cmc/C_{20}
1,2-decanediol	3.63	48.6	9.6
1,3-undecanediol	3.59	48.4	8.9
1,2-dodecanediol	4.55	49.3[a]	6.5
1,3-tridecanediol	4.71	48.3[a]	6.8
1,3-pentadecanediol	5.77	45.5	7.7
$C_8H_{17}OC_2H_4OH$[b]	3.17	45.0	7.2

[a] Below Krafft point; supersaturated solution. [b] K. Shinoda, T. Yamanaka, and K. Kinoshita, *J. Phys. Chem.*, 63, 648 (1959).

From the data in Table I, both the 1,2- and 1,3-alkanediols appear to be oriented at the aqueous solution/air interface in an almost close-packed arrangement of their hydrophilic head groups with both oxygen atoms in the interface and with their alkyl chains more or less perpendicular to it.

Efficiency and Effectiveness of Adsorption. Table II lists the values of the efficiency of surface tension reduction,[3] measured by the negative log of the bulk phase concentration of surfactant required to produce a surface pressure, π, of 20 mN m^{-1} (pC_{20}), the effectiveness of surface tension reduction,[4] measured by the surface pressure at the cmc (π_{cmc}), and the cmc/C_{20} ratio, where C_{20} is the bulk phase concentration of surfactant required to produce a 20 mN m^{-1} reduction in the surface tension of the solvent. The cmc/C_{20} ratio is a measure of the tendency of the surfactant to adsorb at the solution/air interface relative to its tendency to form micelles; the larger the cmc/C_{20} ratio, the larger its adsorption tendency relative to its micellization tendency. For comparison, the corresponding values for $C_8H_{17}OCH_2CH_2OH$, which is isomeric with 1,2-decanediol, are included.

From Figure 1 and Tables I and II it appears that the 1,3-alkanediols are very similar in their adsorption and micellization properties to the 1,2-alkanediols with one less carbon atom. This would imply that the methylene group between the hydroxyl-bearing carbons in the 1,3-diols is not removed significantly from contact with the aqueous phase in adsorption at the aqueous solution/air interface or in micelle formation in aqueous medium. This is consistent with the distinctly lower adsorption efficiency and higher cmc of the 2-octoxyethanol compared to the isomeric 1,2-decanediol, which imply that in the former compound the two carbon atoms between the two oxygen atoms of the hydrophilic group are also not completely removed from contact with the aqueous phase.

TABLE III: Standard Free Energies of Adsorption at the Aqueous Solution/Air Interface at 25 °C

compound	pC_{20}	$\Delta G_{ad}°$, kJ mol^{-1}	$\Delta G_{ad}°$ (W–), kJ mol^{-1}
1,2-decanediol	3.63	-24.5_0	+4.3 ($HOCH_2CHOH-$)
1,3-undecanediol	3.59	-24.0_8	+4.7 ($HOCH_2CH_2CHOH-$)
1,2-dodecanediol	4.55	-29.4_0	+5.2 ($HOCH_2CHOH-$)
1,3-tridecanediol	4.71	-30.1_5	+4.4 ($HOCH_2CH_2CHOH-$)
1,3-pentadecanediol	5.77	-35.9_0	+4.5 ($HOCH_2CH_2CHOH-$)
$C_8H_{17}OCH_2CH_2OH$	3.17	-21.8_6	+6.9 ($HOCH_2CH_2O-$)

TABLE IV: Standard Free Energies of Micellization in Aqueous Solution at 25 °C

compound	log cmc	$\Delta G_m°$, kJ mol^{-1}	$\Delta G_m°$(W–), kJ mol^{-1}
1,2-decanediol	-2.64_5	-18.8_8	+10.7 ($HOCH_2CHOH-$)
1,3-undecanediol	−2.64	-18.6_7	+10.9 ($HOCH_2CH_2CHOH-$)
1,2-dodecanediol	−3.74	-24.7_7	+10.8 ($HOCH_2CHOH-$)
1,3-tridecanediol	−3.85	-25.2_4	+10.3 ($HOCH_2CH_2CHOH-$)
1,3-pentadecanediol	−4.89	-30.8_8	+10.7 ($HOCH_2CH_2CHOH-$)
$C_8H_{17}OCH_2CH_2OH$	−2.31	-16.9_5	+12.6 ($HOCH_2CH_2O-$)

The 1,2-decanediol also shows a greater effectiveness of surface tension reduction, π_{cmc}, than the isomeric $C_8H_{17}OC_2H_4OH$. Since π_{cmc} is well approximated by the equation[4]

$$\pi_{cmc} = 20 + 2.303RT\Gamma_{max} \log (cmc/C_{20})$$

and the Γ_{max} values of the two compounds are almost identical, the greater effectiveness of the former compound is due to its greater cmc/C_{20} ratio.

Standard Free Energies of Adsorption and Micellization. Standard free energies of adsorption, $\Delta G_{ad}°$, at the aqueous solution/air interface were calculated by use of the equation[5]

$$\Delta G_{ad}° = -2.303RT[pC_{20} + 0.22 - \log V_M]$$

where V_M is the molecular volume of the surfactant molecule in nm^3, as calculated from bond lengths[6] and molecular models. This is based upon the formulation of the adsorption equilibrium as

$$C \rightleftharpoons (C)_{ad}$$

with $K_{eq} = [C_{ad}]/[C]$, where the brackets indicate activities of the various species.

The standard state of the adsorbed solute is defined[5] as a hypothetical liquid monolayer of the surface-active solute at 20 mN m^{-1} surface pressure with an activity of 1 mol dm^{-3}. Under the condition of constant surface pressure and temperature in the surface phase and at the low bulk phase concentrations used, it is assumed that activity coefficients in both phases can be neglected. Then,

$$[C_{ad}] = 10^{24}/(V_M \cdot N)$$

where N is Avogadro's number, and $\log K_{eq} = \log [10^{24}/(V_m N C_{20})] = pC_{20} + 0.22 - \log V_M$.

Standard free energies of micellization, $\Delta G_m°$, in analogous fashion were calculated by

$$\Delta G_m° = -2.303RT[0.22 - \log V_M - \log \text{cmc}]$$

defining the standard state for the micellized solute as a micelle consisting of a monomolecular film of surface-active solute with an activity of 1 mol dm^{-3}.

Molecular volumes (V_M), in nm^3, used in calculating $\Delta G_{ad}°$ and $\Delta G_m°$ were as follows: 1,2-decanediol, 0.361; 1,3-undecanediol, 0.389; 1,2-dodecanediol, 0.417; 1,3-tridecanediol, 0.445; 1,3-pentadecanediol, 0.502. Standard free energies of adsorption at the aqueous solution/air interface and standard free energies of micellization in aqueous solution at 25 °C, calculated in the manner described above, are listed in Tables III and IV, respectively.

From the standard free energies of adsorption of the 1,3-alkanediols, the $\Delta G_{ad}°$ per methylene group is -2.8_8 kJ, in good agreement with the value of -2.9_0 kJ obtained from data on C_4–C_8 primary alcohols at 25 °C by use of the same method and a value of -2.8_9 kJ obtained from the same data on C_4–C_8 primary alcohols by the Traube's constant method.[5] From the standard free energies of the two 1,2-alkanediols, the $\Delta G_{ad}°$ per methylene group is -2.4_5 kJ, which may reflect some inaccuracy in the data for one of these compounds.

Using $\Delta G_{ad}°(-CH_2) = 2.9$ kJ and using $\Delta G_{ad}°(CH_3-) = \Delta G_{ad}°(-CH_2-) -5.56$ kJ on the basis of solubility data for liquid n-alkanes in water at 25 °C,[7,8] we calculated standard free energies of adsorption, $\Delta G_{ad}°$(W–), for the hydrophilic groups $HOCH_2CHOH-$ and $HOCH_2CH_2CHOH-$. These values are also listed in Table III, together with standard free energy values calculated in the same fashion for $C_8H_{17}OCH_2CH_2OH$ by using $V_M = 0.363$ nm^3. The $\Delta G_{ad}°$(W–) values for the $HOCH_2CHOH-$ and $HOCH_2CH_2CHOH-$ groups all fall in the range from +4.3 to +5.2 kJ, indicating no essential difference in the hydrophilic character of these two groups, presumably because the methylene group between the two hydroxyl groups in the 1,3-diols is not removed significantly from the aqueous phase. The $HOCH_2CH_2O-$ group of $C_8H_{17}OCH_2CH_2OH$ shows a somewhat larger hydrophilic character (+6.9 kJ). A possible explanation is that the ethereal oxygen, presumably H-bonded to the hydrogens of the water molecules, prevents the methylene between it and the $-CH_2OH$ group from being removed from the aqueous phase. On the other hand, in $HOCH_2CHOH-$, the group can be H-bonded via hydrogen atoms of its hydroxyl groups to the oxygens of the water molecules, thus allowing greater removal of the methylenes in the grouping from the aqueous phase. It is noteworthy in this regard that the $\Delta G_{ad}°$ of the $-OH$ group in a primary alcohol is +7.1 kJ,[5] indicating that the hydrophilic character of the $HOCH_2CH_2O-$ grouping is due almost entirely to the $-OH$ present.

From the standard free energies of micellization listed in Table IV, the $\Delta G_m°$ per $-CH_2-$ is -2.9_5 kJ from the data on 1,2-alkanediols and -3.0_5 kJ from the data on 1,3-alkanediols. Values at 25 °C of −3.03 kJ per $-CH_2-$ are given by Shinoda[9] for alkyl glucosides and −2.85 kJ by Molyneux et al.[8] for the series $R(OC_2H_4)_6OH$. When a value of −3.0 kJ per $-CH_2-$ was used, standard free energies of micellization for the hydrophilic groups, $\Delta G_m°$(W–), were calculated by using $\Delta G_m°(CH_3-) = \Delta G_m°(-CH_2-) -5.56$ kJ.[8] These values are listed in Table IV, together with standard free energies of micellization for $C_8H_{17}OCH_2CH_2OH$. The $\Delta G_m°$(W–) values for the $HOCH_2CHOH-$ and $HOCH_2CH_2CHOH-$ groups all fall in the range from +10.3 to +10.9 kJ, indicating, as shown above for adsorption at the aqueous solution/air interface, no essential difference in the hydrophilic character of these two groups.

The $\Delta G_m°$(W-) values are considerably more positive than the $\Delta G_{ad}°$(W-) values for these two groups, indicating a greater energy barrier to micellization in aqueous solution than to adsorption at the aqueous solution/air interface. This may be due to the steric factor in micellization noted previously.[10] The bulky, hydrated hydrophilic group is probably better accommodated at the planar aqueous solution/air interface than at the micellar surface which is convex to the aqueous solution. As a result, it probably must either dehydrate to a greater extent to fit into the more constricted micelle or remain more deeply immersed in the aqueous phase, with the consequent greater contact of the adjacent carbon atoms with the aqueous phase. Again, as in adsorption at the aqueous solution/air interface, the standard free energy value of the $HOCH_2CH_2O$- group is somewhat more positive than the value for the diol groups.

Acknowledgment. This work was supported in part by a grant from the Pilot Chemical Company of California.

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Intermolecular Charge-Transfer Complexes of Macrocyclic Polyethers with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone

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The interactions of benzo-15-crown-5, dibenzo-18-crown-6, and dibenzo-24-crown-8 with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone have been studied in methylene chloride by using spectroscopic methods. These crown ethers from 1:1 molecular complexes with the acceptor. The magnitudes of association constants and thermodynamic parameters of complexation are indicative of cooperative interaction of oxygens with the acceptor.

Introduction

Macrocyclic polyethers, widely referred to as crown ethers, exhibit many interesting properties. The presence of cavities in these ethers, provided by the cyclic disposition of oxygens, confers unique ligational properties. The ion complexation behavior of these ethers has been well-investigated.[1] The ability of these ethers to act as hosts toward a variety of hydrogen-donating molecules has been reviewed by Cram and Cram.[2] The forces that govern the interaction of two molecules in a given geometry arise from dipole-dipole, dipole-induced-dipole, and other long-range coupling effects. Morakuma[3] reviewed the various factors contributing to the ground-state stabilization of fairly strong molecular complexes and concluded that though the major contribution arose from electrostatic effects the charge-transfer forces played a small but significant role in the stabilization. The present study reported here on the interaction of crown ethers with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) is carried out to determine the nature of forces responsible for stabilization of the complexes in solution and the relative orientations of the donors and acceptor.

The benzene-substituted ethers 2,3-benzo-1,4,7,10,13-pentaoxacyclopentadec-2-ene (benzo-15-crown-5), 2,3:11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene (dibenzo-18-crown-6), and 2,3:14,15-dibenzo-1,4,7,10,13,16,19,22-octaoxacyclotetracosane-2,14-diene (dibenzo-24-crown-8) were chosen for the study (Figure 1). The hole diameters of the ethers range from 0.17 to 0.58 nm. The ethers possess both n and π sites for donation. DDQ is one of the strong acceptors, and many of its complexes with π donors are known.[4] Electronic spectral methods have been used to evaluate association constants and thermodynamic parameters of complexation. The $-OCH_2CH_2O-$ groups of the ethers are capable of existence in various conformations, and ^1H NMR measurements are of significance here to determine any favored orientations of the ethers in the complexes. The results of these studies are informative in arriving at the nature of stabilization forces (n-π or π-π type) and the presence of any coordinative or simultaneous interactions of oxygen and benzene rings with DDQ.

Experimental Section

The benzene-substituted ethers benzo-15-crown-5, dibenzo-18-crown-6, and dibenzo-24-crown-8 were synthesized according to published procedures.[5] DDQ was obtained from Koch Light, England, and twice crystallized from benzene (mp 215 °C). B.D.H. reagent grade methylene chloride was used as the solvent. It was washed with 10% sodium carbonate solution followed by distilled water, dried over fused calcium chloride for 24 h, and distilled.

A Unicam SP 700A double-beam spectrometer fitted with a pair of matched quartz cells of 1-cm path length was used for spectral measurements. The temperature of the quartz cells was maintained at a set temperature (±0.05 °C) by circulating cooling liquid from an external unit. The ^1H NMR spectra of the complexes were recorded on a Bruker WH 270-MHz FT NMR spectrometer, using $CDCl_3$ as a solvent and Me_4Si as an internal standard.

Stock solutions of (50 mL) of ethers (0.2 M) and DDQ (0.001 M) in dry methylene chloride were prepared by