two volumes of ethanol was added to the clear supernatant. The precipitated barium thymidine 5′-phosphate was successively washed with ethanol, acetone, and ether (yield 47.0%). The product was chromatographically homogeneous.

Similarly, the reaction of uridine with I, II, and III resulted in the formation of uridine 5′-phosphate in 27.8% yield. The product was isolated as its barium salt and identified by paper chromatography. When the reaction was carried out in dioxane at 60°, the yield of uridine 5′-phosphate was increased to 63%. The ultraviolet absorption characteristics of the products and the R_f's of different compounds are listed in Tables I and II, respectively.

Table I. Ultraviolet Absorption Characteristics

	OD_{290}/OD_{260}	OD_{280}/OD_{260}	OD_{250}/OD_{260}
Thymidine 5′-phosphate (pH 7.0)	0.23	0.71	0.65
Uridine 5′-phosphate (pH 4.8)	0.017	0.38	0.73

Table II. Paper Chromatography of Different Compounds[a]

	R_f	
Compounds	Solvent I	Solvent II
Thymidine 5′-phosphate	0.70	
Thymidine 3′-phosphate	0.83	
Uridine 5′-phosphate		0.22
Uridine 3′(2′)-phosphate		0.31

[a] Paper chromatography was performed by the ascending technique using Toyo Roshi No. 51A paper. The solvent systems used were solvent I, 1-propanol-2 *N* HCl (5:1); solvent II, 1-propanol-concentrated NH_4OH-H_2O (6:3:1).

Although the yields of thymidine 5′- and uridine 5′-phosphates were not high, no isomeric 3′- and/or 2′-phosphates could be detected in the debenzylated products by paper chromatography. As expected, this result and other work in the related fields show that steric factors are of importance for the selective phosphorylation. Work is continuing to find optimum conditions of the method as well as further development of the present system.

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Micelle Formation in Pure Ethylene Glycol[1]

Sir:

Ethylene glycol plays an important role in protein conformation studies[2–6] because it is a weak protein denaturant compared to urea or other organic solvents such as ethanol, dioxane, etc. However, at low or intermediate concentrations, it does weaken hydrophobic bonding in model systems[7–12] including those containing ionic[8–11] and nonionic[10,12] detergent micelles in water.

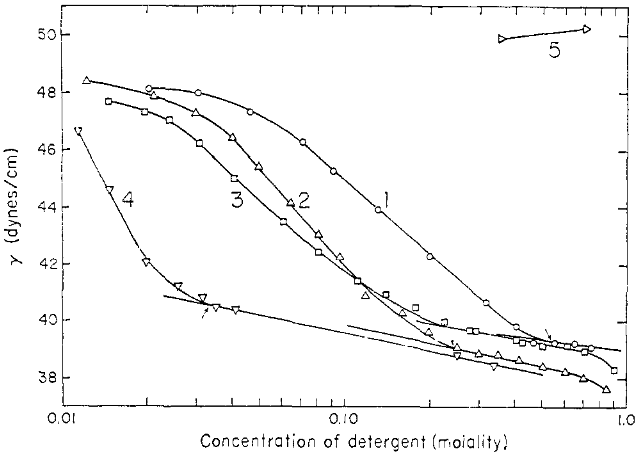

Figure 1. The variation of surface tension, γ, with the logarithm of concentration: (○) DPB, (△) MTAB, (□) CPC, and (▷) EPB, in pure ethylene glycol; (▽) DPB in 40 vol % ethylene glycol.

Although the limited solubility of hydrocarbons in pure ethylene glycol in contrast to their complete miscibility with ethanol or dioxane[13] and the close resemblances between ethylene glycol and water in many of their properties would indicate that hydrophobic or, more correctly, lyophobic bonding may still persist in pure ethylene glycol, no report seems to have appeared so far demonstrating the existence of micelles in this solvent. As is well known, the formation of detergent micelles in water provides an excellent example of hydrophobic bond formation.

The present work reports the determination of what appear to be the critical micelle concentrations (cmc's) of three cationic detergents of three different chain lengths, *viz.* dodecylpyridinium bromide (DPB), myristyltrimethylammonium bromide (MTAB), and cetylpyridinium chloride (CPC) in pure ethylene glycol. No such determination was possible in the case of another detergent, cetyltrimethylammonium bromide (CTAB), a higher homolog of MTAB, because of the surprisingly low solubility of CTAB in ethylene glycol at room temperature.

Chromatoquality reagent grade ethylene glycol (EG), purchased from Matheson Coleman and Bell, was dried with anhydrous Na_2SO_4 and distilled under reduced pressure before use.

The method used involved the measurements of surface tensions of detergent solutions using a Rosano surface tensiometer. About 10 ml of solution was used for each measurement, and the time allowed for equilibration varied between 5 and 20 min, during which the solutions were kept covered with aluminum foil. The measurements were carried out at 27.5 ± 0.5°.

Figure 1 shows plots of surface tension (γ) *vs.* logarithm of concentrations for the three detergents and

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(1) This work was supported by the National Science Foundation under Grant No. GB-8410, held by Professor G. Némethy.

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ethylpyridinium bromide (EPB) in pure EG. A similar plot for DPB in 40 vol % EG is also included in this figure, as DPB is known to form micelles in this solvent mixture.[11] A comparison of curve 4 with curves 1–3 indicates that the processes occurring in the two solvents are very similar. The positions of the cmc's on these curves are indicated by the arrows. The cmc so obtained for DPB in 40 vol % EG, 0.033 *m*, agrees well with the value, 0.0332 *m*, obtained by a spectrophotometric technique.[11,14,15] The cmc values are listed in Table I and are found to increase by factors of 45, 65, and 250 for DPB, MTAB, and CPC, respectively, in going from water to EG.

Table I. Cmc Data at 27.5°

Detergent	Cmc in water,[a] *m*	Cmc in pure EG, *m*	$\text{Cmc}_{\text{EG}}/\text{cmc}_{\text{H}_2\text{O}}$
DPB	1.22×10^{-2} [b]	0.55	45
MTAB	3.84×10^{-3} [c]	0.25	65
CPC	9.2×10^{-4} [c]	0.23	250

[a] Calculated from the values at 25° assuming roughly 1% increases in going from 25 to 27.5°, which appears to be reasonable.[11] [b] References 15 and 11. [c] Reference 10.

Unlike the long-chain (lc) electrolytes, ethylpyridinium bromide (EPB), a shorter chain analog of DPB, clearly raised the surface tension of EG (48.9), thus resembling NaCl in water[16a] in its behavior. This proves beyond any doubt that the pronounced surface activities of the lc electrolytes in EG are caused by the long hydrocarbon chains of these compounds, and not by any ion pairing, as the latter can be shown to occur to about the same degree in EPB and DPB in pure EG.[11]

However, a calculation of the surface excess,[16b] Γ_2, in the concentration region where there is the sharpest decrease in the surface tension, using the equation

$$\Gamma_2 = -\frac{1}{RT}\frac{d\gamma}{d\ln C} \tag{1}$$

shows that in 40 vol % EG Γ_2 is comparable to the values available for other detergents in water, whereas in pure EG these values are reduced by about a factor of 3. This would suggest that surface activity, although clearly existent, is considerably reduced in pure EG compared to that in water or 40 vol % EG.

An independent piece of evidence in favor of micelle formation in EG could be provided by the observation that at room temperature the solubility of CTAB in this solvent is lower by a factor of 10 or more than that of MTAB, although the hydrocarbon chain, supposed to be organophilic, is longer by two C atoms in the former. Also, preliminary measurements indicate that the solubility of CTAB in EG increases sharply in the temperature range 32–35°. This points to the possible existence in this solvent of a temperature similar to the Kraft temperatures known to exist for detergents in water.[16c]

The most likely conclusion will, therefore, be that micellar aggregation does take place in pure EG, although nothing is known yet as to how large these micelles are. To the knowledge of the present author, this is the first report ever made about the possible existence of micelles in any pure polar organic solvent.[17] More detailed investigations of this phenomenon are in progress in this laboratory.

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(17) "Inverted" micelles are, however, known to form in some nonpolar solvents such as benzene, toluene, *n*-heptane, *n*-decane, etc.

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Molecular and Electronic Structure of μ-Nitrogen-decaamminediruthenium(II)

Sir:

The binuclear ruthenium complex $[Ru(NH_3)_5N_2Ru(NH_3)_5](BF_4)_4$, recently isolated by Harrison, Taube, and Weissberger,[1] apparently contains molecular nitrogen as a bridging ligand and thus is of considerable theoretical interest. Not only does it serve as a simple model for the biological nitrogen fixation process, but it is of general importance in understanding the interactions between metal atoms and π-acceptor ligands. More particularly, it is an important link in the interesting class of binuclear compounds which contain simple diatomic bridging ligands such as $O_2^{-\ 2}$ and CN^-.[3]

The crystals used in our study were prepared by the literature procedure.[1] Following the addition of KBF_4, the reactants were allowed to stand under N_2 for 4 days. After this period, small, golden yellow, octahedral crystals were found under an excess of KBF_4; a number were separated, washed with ethanol, and mounted on glass fibers for X-ray diffraction studies.

Weissenberg photographs (Cu Kα radiation) showed the crystals to be orthorhombic, the extinctions indicating the space group D_{2h}^{15}-Pbca. The cell constants are $a = 12.78$, $b = 15.53$, $c = 13.34$ Å. The observed density (flotation) of 1.96 g/cm^3 is in good agreement with the value of 1.97 g/cm^3 calculated for 4 dimeric cations, 16 BF_4^- anions, and 8 water molecules per unit cell. In this space group, the cations must lie on centers of symmetry.

Intensity data for 3040 independent reflections were collected on a Datex-automated General Electric XRD-6 diffractometer, using zirconium-filtered Mo Kα radiation. The structure was determined by Patterson and Fourier methods and refined using full-matrix least-squares techniques. In the final cycles, all atoms except the hydrogens were assigned anisotropic temperature factors. The refinement proceeded to a final *R* factor ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.090 and a goodness of fit $(\Sigma w(F_o^2 - F_c^2/k^2)^2/(m - S))^{1/2}$ of 1.63.

The dimeric cation is shown in Figure 1. The RuN_2Ru unit is very nearly linear (the Ru–N–N angle is 178.3 (5)°); the Ru–Ru distance is 4.979 (2) Å and

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