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VISIBLE SPECTRA OF DICARBONYL SUBSTITUTED
TRIS-BIPYRIDYL RUTHENIUM (II) COMPLEXES

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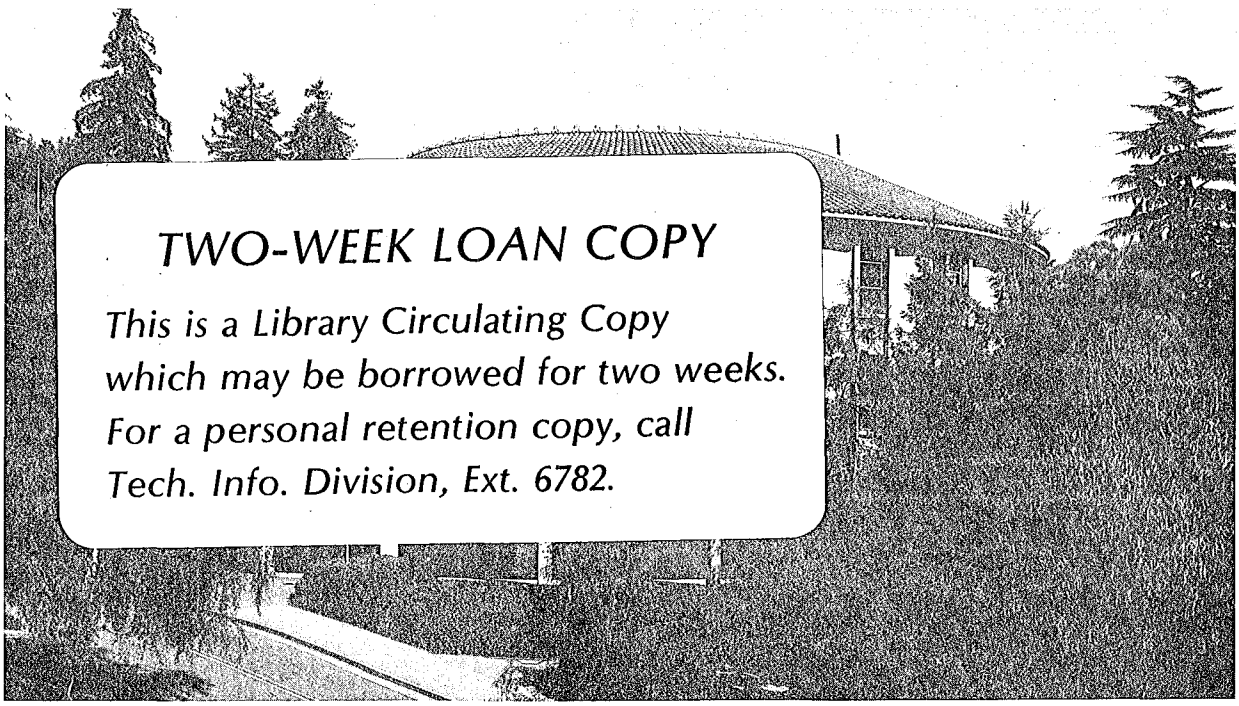

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VISIBLE SPECTRA OF DICARBONYL SUBSTITUTED TRIS-BIPYRIDYL RUTHENIUM (II) COMPLEXES

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ABSTRACT

The solvent dependence of the metal-to-ligand charge transfer band pattern of tris-bipyridyl ruthenium(II) derivatives with carbonyl substituents is attributed to a reduction in the energy required for electron transfer to the dicarbonylated bipyridyl ligand with an increase in solvent polarity.

The mixed-ligand dialkyl carboxylic acid ester derivatives of the tris(2,2'-bipyridyl)ruthenium(II) complex (abbreviated to $[Ru(bipy)_3]^{2+}$), which were first prepared and characterized by Sprintschnik, et al. [1], have a marked solvent dependence of their optical absorption and emission spectra [2-8] compared to the parent complex. The diketone analogue prepared by Johansen, et al. [8] exhibits similar solvent-dependent spectra [8], as does the dicarboxamide derivative prepared by us (Fig. 1) [9]. The three mixed-ligand analogues will be abbreviated as $[(bipy)_2Ru(bipy\text{-}COR)]^{2+}$ (R= $-OC_{18}H_{37}$, $-C_{18}H_{37}$, or $-NHC_{16}H_{33}$), where the two carbonyl substituents are located in the para (4,4') positions of one of the bipyridine ligands. Transfer of $[(bipy)_2Ru(bipy\text{-}COR)]^{2+}$ from an aqueous solvent to an organic solvent causes the visible metal-to-ligand charge transfer absorption band with two maxima to collapse into a band with a single peak, and the emission maximum blue-shifts. The long-chained ruthenium complexes are promising as electron-transfer photosensitizers in solar energy-converting devices [1-13], so it is important to understand the effect of solvent on their electronic structures, as reflected by their spectra. Johansen, et al. [8] considered the possibility that the absorption spectra indicated changes in the state of aggregation of the dicarbonylated complexes. In this letter we suggest that the solvent dependence of the spectra of $[(bipy)_2Ru(bipy\text{-}COR)]^{2+}$ arises from stabilization of the charge transfer excited state relative to the ground state by increasing solvent polarity.

Spectral changes associated with transfer of $[(bipy)_2Ru(bipy\text{-}COR)]^{2+}$ from aqueous to organic solvents bear a striking resemblence to the changes associated with deprotonation of the carboxylic acid

substituents of $[(bipy)_2Ru(bipy\text{-}COOH)]^{2+}$ [2,3,7,14]. The absorption and emission spectra of $[(bipy)_2Ru(bipy\text{-}\ COHNC_{16}H_{33})]^{2+}$ dissolved in chloroform and in aqueous detergent solution, which represent the extreme cases that we have observed for this complex, are reproduced in Fig. 2. (Four absorption bands have been labeled I to IV for sake of discussion.) For comparison, the absorption spectra of the protonated and ionized forms of $[(bipy)_2Ru(bipy\text{-}COOH)]^{2+}$ in aqueous solution are shown in Fig. 3. The correspondence between the changes in absorption spectral patterns of the two complexes indicates that the perturbations of the electronic structures of the complexes were similar in both cases and implicates a role of the carbonyl substituents.

← Fig. 2

← Fig. 3

The absorption spectrum of $[(bipy)_2Ru(bipy\text{-}\ CONHC_{16}H_{33})]^{2+}$ in other solvents had characteristics intermediate to the two extremes of Fig. 2. A plot of the frequency of the long-wavelength peak of band I ($\bar{\nu}^{I}_{max}$) versus the dielectric constant of the solvent, as a measure of solvent polarity, indicated that aqueous solvents were exceptional. However, the plot of $\bar{\nu}^{I}_{max}$ versus the Hildebrand solubility parameter [15], which is currently the most widely applied index of solvent polarity [15], was roughly linear, including points corresponding to aqueous media (Fig. 4). There was a poor correlation between $\bar{\nu}^{I}_{max}$ and either Kosower's [16] Z- or Reichardt's [17] E_T-values. Unfortunately, no single parameter can be used to characterize solvent polarity [17]. Nevertheless, the results indicate that the effect of solvent on the spectrum of $[(bipy)_2Ru(bipy\text{-}\ CONHC_{16}H_{33})]^{2+}$ was mainly one of polarity, with no specific solvent complex interactions (eg. hydrogen bonding) being obvious.

← Fig. 4

The decrease in $\bar{\nu}^{I}_{max}$ with increasing solvent polarity implies

that the lowest photoexcited state of $[(bipy)_2Ru(bipy\text{-}CONHC_{16}H_{33})]^{2+}$ has a greater dipole moment than does the ground state of the complex [17], which is consistent with the metal-to-ligand (d_π,π^*) charge transfer assignment for the visible absorption bands of $[Ru(bipy)_3]^{2+}$ and related complexes [18-21]. The charge transfer configuration of $[Ru(bipy)_3]^{2+}$ is viewed as having a Ru^{3+} core coordinated to a bipyridine anion radical [20]. The optically transferred electron in photoexcited $[(bipy)_2Ru(bipy\text{-}CONHC_{16}H_{33})]^{2+}$ can presumably reside on either the bipy or bipy-$CONHC_{16}H_{33}$ ligands. In the latter case, resonance forms can be drawn in which the electron is on the oxygen atom of one of the amide substituents. Therefore the dipole moment of the (d_π, π^*(bipy-$CONHC_{16}H_{33}$)) excited state is greater than that of the (d_π, π^*(bipy)) state, the difference depending on the relative contribution of carbonyl-localized electron configurations. In the case of $[(bipy)_2\text{-}Ru(bipy\text{-}COOH)]^{2+}$, deprotonation of the carboxylic acid would be expected to disfavor localization of the optically promoted electron on the carbonyl oxygen atoms. In view of the similarities in the the two extreme absorption patterns exibited by $[(bipy)_2Ru(bipy\text{-}COOH)]^{2+}$ and by $[(bipy)_2Ru(bipy\text{-}CONHC_{16}H_{33})]^{2+}$ (Figs. 2 and 3), the effect of increasing solvent polarity on the spectrum of the latter can be attributed to making more favorable charge transfer configurations with the promoted electron on one of the carbonyl oxygen atoms, which have greater dipole moments than do configurations with the electron on one of the pyridyl rings.

The changes in absorption bands II and III that accompany changes in band I in Figs. 2 and 3 support involvement of the carbonyl substituents. Band II has been assigned to the transition involving

electron transfer from Ru(II) (d orbital) to the second lowest π^* orbital of bipy [18]. Both charge transfer bands I and II red-shift by ~1 kK, supporting that assignment. Band III is the composite of the main intraligand (π,π^*) transitions [18,22-23]. The shoulder near 305 nm is due to the bipy-$CONHC_{16}H_{33}$ ligand, and the increased prominence of the shoulder that accompanies the red shifts of bands I and II further implicates a role of the carbonyl substituents in the spectral changes shown in Figs. 2 and 3.

We therefore contend that the solvent dependence observed by us [9] and others [2-8] of the visible and ultraviolet absorption spectra of dicarbonyl substituted derivatives of $[Ru(bipy)_3]^{2+}$ arises mainly from stabilization of the (d_π,π^*(bipy-COR)) transitions relative to the (d_π,π^*(bipy)) transition. The changes in the visible absorption band patterns can to some extent be accounted for by assuming that the charge transfer absorption bands are, approximately, composites of bands due to individual Ru(II)-ligand interactions [4,24]. Thus, the spectral pattern of $[Ru(bipy)_3]^{2+}$ is relatively insensitive to solvent because the three (d_π,π^*) transitions are equally affected.

A practical consequence of the solvent dependence of the spectrum of $[(bipy)_2Ru(bipy\text{-}CONHC_{16}H_{33})]^{2+}$ is that the polarity of the environment of the chromophore can be assessed from the shape of the spectrum. The absorption spectrum of this complex dissolved in phosphatidylcholine bilayer vesicle dispersions [10,12] resembles the spectrum of the complex in other aqueous media (points labeled a to e in Fig. 4), so we infer that the dye molecules are oriented in the vesicles like the phospholipid molecules, with their charged chromophores located near the bilayer-water interface.

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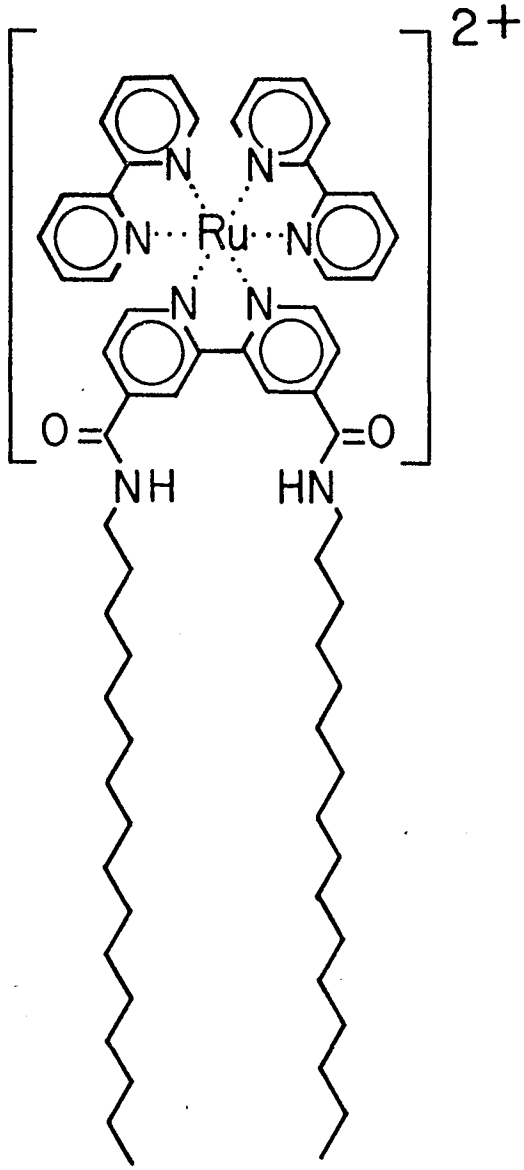
FIGURE LEGENDS

Figure 1. Structural formula of $[(bipy)_2Ru(bipy\text{-}CONHC_{16}H_{33})]^{2+}$.

Figure 2. Absorption (—) and emission (- -) spectra of $[(bipy)_2Ru(bipy\text{-}CONHC_{16}H_{33})](ClO_4)_2 \cdot H_2O$ dissolved in chloroform and in aqueous detergent solution. The detergent (0.010 M) is $CH_3(CH_2)_{15}N^+(CH_3)CH_2CH_2CH_2SO_3^-$. The emission spectra are uncorrected.

Figure 3. Absorption spectra of the ionized and protonated forms of $[(bipy)_2Ru(bipy\text{-}COOH)](PF_6)_2$ dissolved in aqueous 1.0 M KCl solution. Upper trace : pH = 5.84. Lower trace: pH = 1.05 (pH adjusted with concentrated HCl).

Figure 4. Plot of the peak frequency of the visible charge transfer band (I) of $[(bipy)_2Ru(bipy\text{-}CONHC_{16}H_{33})]\ (ClO_4)_2 \cdot H_2O$ versus the Hildebrand solubility parameter of the solvent. Points a to e correspond to the complex dispersed in the following aqueous media: a, water; b, 0.10 M ammonium acetate; c, the chloride form of the complex in water; d, phosphatidylcholine vesicles; e, in detergent solution. The line was obtained using least-squares analysis including all points except a to e.



$$[(bipy)_2Ru(bipy\text{-}CONHC_{16}H_{33})]^{2+}$$

XBL 806-4226

FIGURE 1
Ford and Calvin

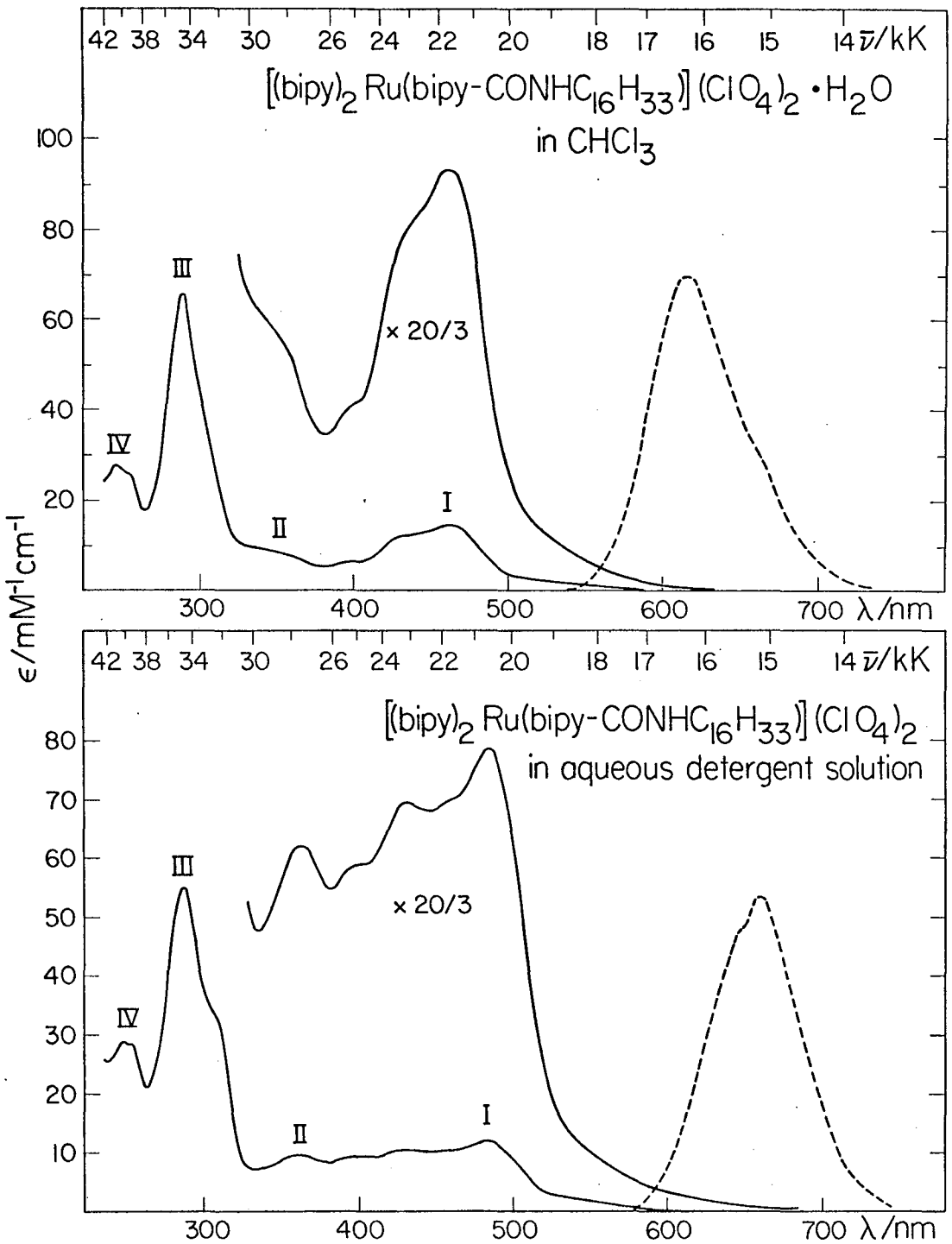


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FIGURE 2

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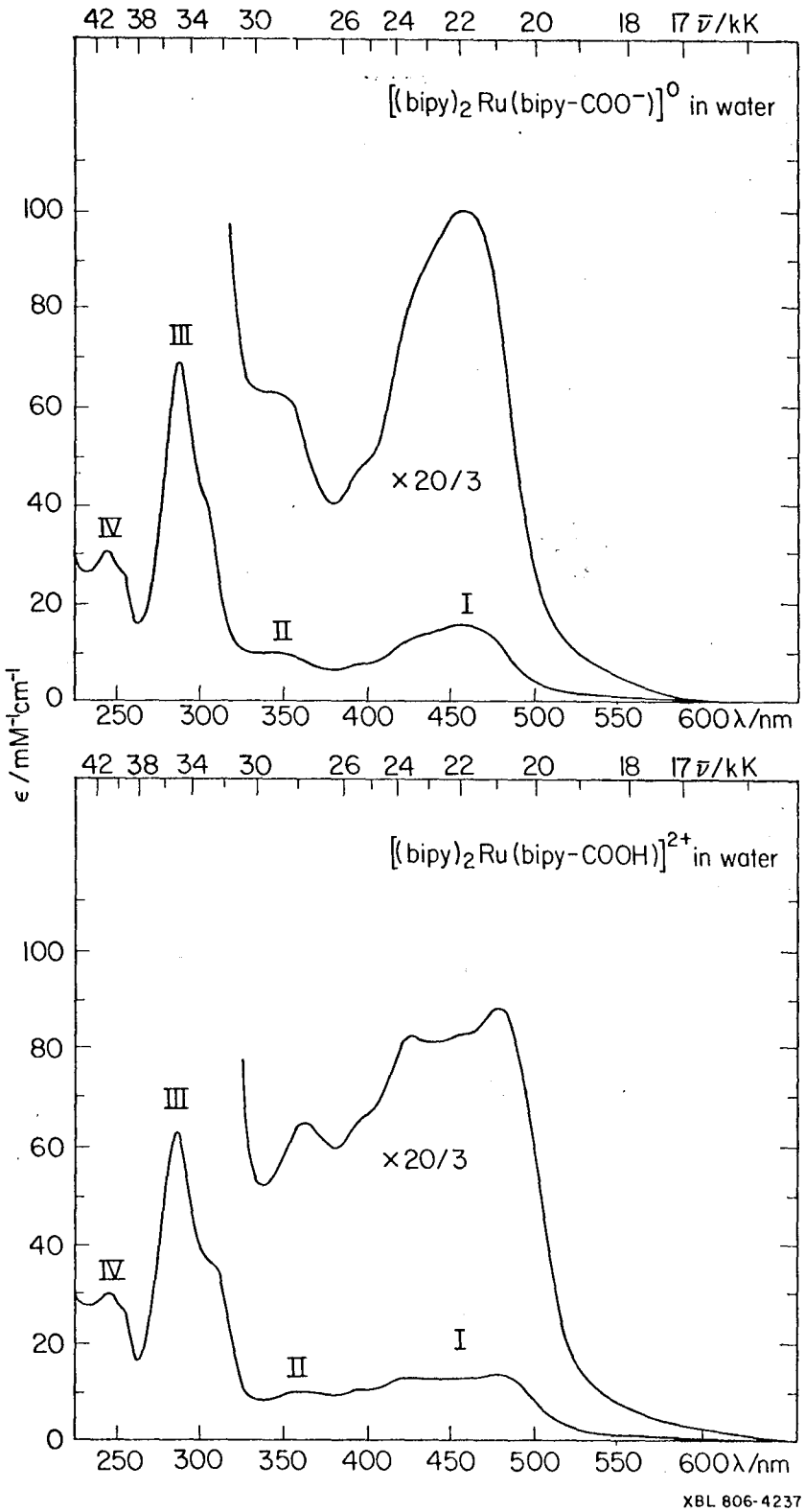
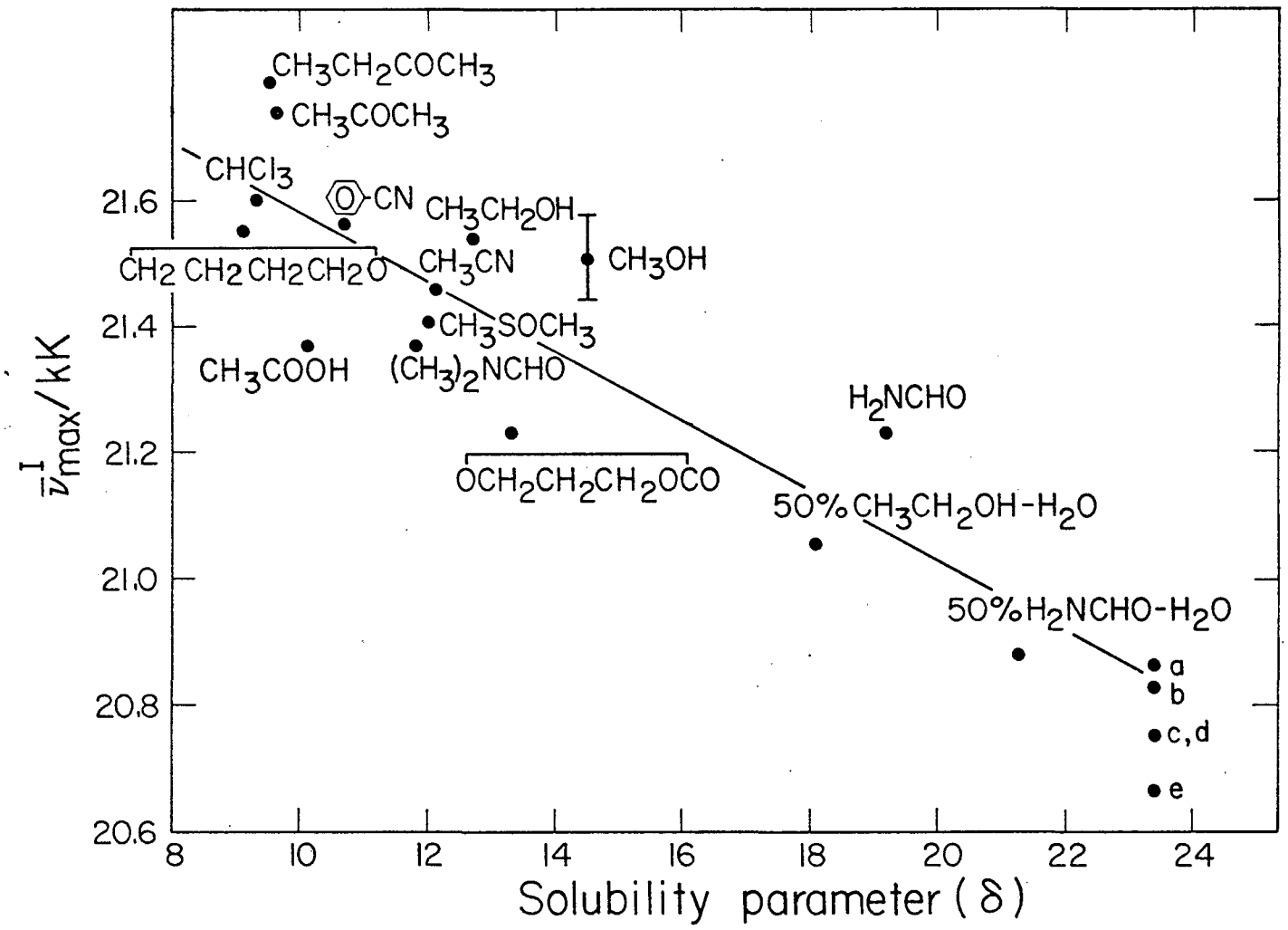


FIGURE 3

Ford and Calvin



XBL 802-4030A

FIGURE 4

Ford and Calvin

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