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CTAB micelles and the hydroformylation of octene with rhodium/TPPTS catalysts Evidence for the interaction of TPPTS with micelle surfaces

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Abstract

The addition of cetyltrimethylammonium bromide (CTAB) to TPPTS/rhodium hydroformylation catalysts has a complicated effect on reaction activity and selectivity. In water alone as the solvent, high CTAB concentration leads to the formation of emulsions and reaction selectivity drops. In aqueous alcohol solvents selectivity also drops but the effect appears to be due to the solvent composition. Emulsion formation is minimized and initial reaction activity goes through a maximum at a CTAB/TPPTS ratio of 3. NMR studies show that there is a strong interaction of CTAB and TPPTS in water while the interaction in aqueous methanol appears to be nonspecific.

Keywords: Octene hydroformylation; Rhodium/TPPTS; Micelles; CTAB

1. Introduction

The use of water-soluble catalysts for hydrogenation and hydroformylation in the aqueous phase is now well recognized as an effective method for catalyst immobilization [1]. Furthermore, it is well established that the method is limited to substrates that have some water solubility. This is particularly true for reactions that require high rates to be economically viable as is the case for commodity chemicals such as aldehydes prepared from olefins. Several research groups have recognized that the addition of surfactants to water-soluble hydroformylation catalysts may extend the biphasic catalysis method to substrates that have poor water solubility [2–7].

In the case of water-soluble hydrogenation catalysis, it is known that surfactants can influence reaction selectivity. For example, the addition of sodium dodecylsulfate to sulfonated chiral bisphosphines leads to improved enantioselectivity in some asymmetric hydrogenation reactions [8–10]. The difference in enantioselectivity with and without the surfactant can be up to 70%.

The preparation of ammonium ion salts of trisulfonated triphenylphosphine (TPPTS) was investigated by Bahrmann et al. [7] and Li et al. [6]. Bahrmann et al. showed that long chain amines and pH control can be used to modify the solubility of TPPTS based catalysts. Significant rate enhancements are observed for the hydroformylation of water insoluble olefins since the ammonium ions behave as surfactants. The concept

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is outlined in Eq. (1). Catalyst immobilization in the aqueous phase is achieved by raising the pH. Also, it was shown that the catalysts can be separated from products by membrane filtration techniques [7].

$$\underset{\text{water soluble}}{(\text{TPPTS})\text{Na}_3} \overset{3\,\text{H}^+}{\rightleftharpoons} (\text{TPPTS})\text{H}_3 \overset{3\,\text{R}_2\text{NH}}{\rightleftharpoons} \underset{\text{lipid soluble (when R is large)}}{(\text{TPPTS})(\text{R}_2\text{NH}_2)_3} \quad (1)$$

Li et al. modified TPPTS based rhodium catalysts by adding the surfactant CTAB, $(C_{16}H_{33})N(CH_3)_3Br$. A typical catalyst consisted of Rh/TPPTS/CTAB in a ratio of 1/16/8 with a CTAB concentration that exceeds the critical micelle concentration (cmc). In all the cases investigated, the TPPTS concentration exceeded the CTAB concentration. Consistent with the observations of Bahrmann et al. and Li et al. find that the activity of the catalysts improves and the selectivity in the hydroformylation reaction, as measured by the linear to branched ratio, decreases slightly [6]. Furthermore, Li et al. showed that the cmc of CTAB drops from approximately 1×10^{-3} to 0.7×10^{-3} M in the presence of TPPTS.

A simple model for the interaction of TPPTS with the surface of micelles of cationic surfactants is illustrated in Fig. 1. At high relative CTAB concentrations it should be possible for TPPTS to interact through all three sulfonate groups. At low relative CTAB concentrations only one or two sulfonate groups per TPPTS on average will interact with the CTAB micelle surface.

The results from Li et al. suggest that he maximum benefit from CTAB addition occurs at about one CTAB per TPPTS. At higher ratios of CTAB the rate does not continue to increase and the percentage of linear aldehyde product formed drops. The model in Fig. 1 indicates that a ratio of CTAB/TPPTS of 3 or higher should maximize the interaction of TPPTS with the micelle surface.

We report the NMR evidence here that supports the strong binding of TPPTS to cationic micelles in water. It is possible that the poor selectivity in the hydroformylation reaction is related to the strong interaction TPPTS with the cationic micelles.

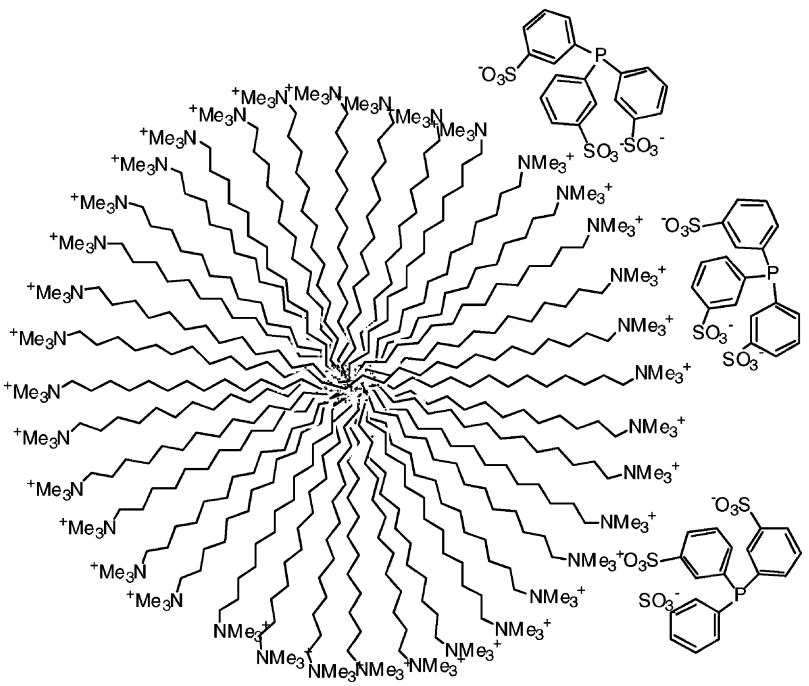

Fig. 1. Schematic illustration of interaction between TPPTS and CTAB micelle surface.

2. Experimental

2.1. General

All the solvents were degassed prior to use by refluxing for several hours under nitrogen. All the manipulations were done using standard Schlenk and syringe techniques under argon. $Rh(acac)(CO)_2$ (98%), tetrabutylammonium bromide (TBAB, 99%), and CTAB (p.a.) were purchased from Aldrich and used as received. The ligand, TPPTS-Cs_3 (tri-cesium triphenylphosphine sulfonic acid) was prepared in accordance with a literature method [11] describing the synthesis of the analog sodium compound, TPPTS-Na_3. The only significant derivation from that procedure was substituting the final neutralizing sodium hydroxide solution with a cesium hydroxide solution [12]. Analytical data of the ligand correlated with previously reported data [12,13].

For hydroformylation reactions standard grade synthesis gas, CO/H_2 (1/1), was used. Reaction product analysis was performed on a HP 6890 gas chromatograph equipped with a HP1 capillary column (25 m × 0.32 mm × 0.52 μm). Detection was done by flame ionization using standard grade H_2 and air with He as carrier gas. The 2-methyloctanal used for GC calibration was prepared according to Nikishin et al. [14]. All the other reagents and solvents were obtained from commercial suppliers in high purity grades and used without further pretreatment or purification.

Most NMR spectra were recorded on a Bruker AM 360 MHz spectrometer in D_2O at 25 °C (^1H NMR: 360.13 MHz. $^{13}C\{^1H\}$ NMR: 90.556 MHz, both referenced to TMS. $^{31}P\{^1H\}$ NMR: 145.785 MHz, referenced to external $P(OPh)_3$ in $CDCl_3$ (capillary tube), $\delta = 128.5$ ppm). Exceptions were ^{31}P NMR spectra recorded to determine diffusion rates. Here spectra were recorded on a Jeol Eclipse + 500 MHz spectrometer in D_2O and in 50/50 vol.% D_2O/CD_3OD mixtures at 25 °C ($^{31}P\{^1H\}$ NMR: 202.468 MHz, referenced to external $P(OPh)_3$ in $CDCl_3$ (capillary tube), $\delta = 128.5$ ppm).

2.2. Diffusion measurements

^{31}P NMR spectra were recorded on D_2O solutions of TPPTS having various contents of the additives, A, TBAB and CTAB. TBAB or CTAB was consecutively added to ligand solutions having [P] = 4.7 and 3.3 mM, giving rise to TBAB and CTAB concentrations that correspond to A/P ratios of 0–20 and 0–50, respectively ([A] = 0–0.24 M). Pulse field gradient (PFG) diffusion rates were measured of species present solutions of (i) D_2O, (ii) D_2O containing TPPTS, (iii) 50/50 vol.% D_2O/CD_3OD containing TPPTS, and (iv) D_2O containing TPPTS together with CTAB (A/P = 15.2).

2.3. Dynamic light scattering

These experiments were performed on aqueous solutions of TPPTS, CTAB and mixed solutions. Hydrodynamic radii were measured for CTAB solutions having [CTAB] = 18.1, 37.2 and 90.5 mM, and for 6.0 mM TPPTS solutions containing various amounts of CTAB corresponding to A/P ratios of 0, 3, 6.2 and 15.1 ([A] = 0, 18.0, 37.2 and 90.6 mM, respectively).

2.4. Hydroformylation catalysis

Aqueous biphasic batch hydroformylation reactions of 1-octene were performed in 30 ml capacity stainless steel high pressure Schlenk tubes. Preformed catalyst solutions having [Rh] = 5.0 mM and [P] = 46.8 mM (P/Rh ratio = 9.4) were made from $Rh(acac)(CO)_2$ and TPPTS in water and 50/50 vol.% water/ROH (R = Me, Et) solutions, respectively, by stirring the solutions for 1 h. For reactions with the additives (A), TBAB or CTAB, the corresponding amount of solid additive necessary to obtain desired A/P ratio was added to the catalyst solutions prior to stirring. The A/P ratios ranged from 0 to 15 ([A] = 0–0.7 M).

In the reactor 1.0 ml of catalyst solution was stirred for 1 h with CO/H_2 gas at 15 bar (220 psig) and 120 °C. After cooling and depressurization 0.75 ml 1-octene and 0.25 ml decane (internal reference) were loaded into the reactor under argon (1-octene/Rh = 956/1). After successively flushing of the reactor with CO/H_2 gas followed by evaporation to vacuum several times, the reactor was re-pressurized with gas to 15 bar. The reaction was started by immersing the reactor into a preheated oil bath ($T = 120$ °C). Thorough mixing of

the phases during reaction was ensured by stirring the mixture at constant rate (500 rpm).

To terminate reaction the reactor was cooled in an ice-water bath for 0.5–1 h followed by slow depressurization. This allowed catalyst and product phases to separate completely in most cases. The product mixtures obtained from reactions performed in water using high additive concentrations (e.g. [CTAB] $\geq$ 0.5 M) had a pronounced tendency to form emulsions. However, no significant difference in product distributions was observed between the upper phase and the emulsion phase in these cases. The presence of alcoholic co-solvents prevented the formation of emulsions in the additive concentration range examined. Samples taken from the upper product phase were subsequently examined by FID–GC analysis.

3. Results and discussion

3.1. Hydroformylation catalysis

The effect of quaternary ammonium ions on the TPPTS/rhodium hydroformylation system was studied in water, aqueous methanol, and aqueous ethanol. In water TBAB, was added, and in the aqueous alcohol solvents CTAB was added. The results shown in Table 1 are representative for the hydroformylation of octene. Generally, selectivity to aldehydes and selectivity to linear versus branched aldehydes drops upon addition of quaternary ammonium bromide salts. It is known that halide ion can have a detrimental effect on hydroformylation catalysis. Thus, the results reported here for CTAB are best viewed in relation to the control experiments with TBAB. Selectivity also drops as the solvent composition changes from water alone to aqueous alcohol. The effect of solvent composition on hydroformylation selectivity in the TPPTS catalyst system is well known.

The relationship of activity and quaternary ammonium ion concentration is more complicated. Octene conversions, at short reaction time, are shown in Figs. 2 and 3 for CTAB addition in aqueous methanol and aqueous ethanol respectively. CTAB first enhances, then diminishes the initial activity of the rhodium/TPPTS catalysts. In all cases the CTAB concentration is well above its critical micelle concentration in water (9.2×10^{-4} M) [15]. (The rhodium concentration is 5.0×10^{-3} M, [TPPTS] = 4.7×10^{-2} M, and [CTAB] = 4.7×10^{-2} to 7.0×10^{-1} M.) The critical micelle concentration of CTAB in aqueous methanol increases substantially, to about 2.5×10^{-2} M [15]. The CTAB concentrations used for the hydroformylation catalysis also exceed this value.

It is informative to plot the results as a function of time at different CTAB/TPPTS ratios. For the reactions in aqueous methanol and ethanol the results are shown in Figs. 4 and 5, respectively. At short reaction times, the effect of the quaternary ammonium ion surfactant is to inhibit the reaction while at longer reaction times the activity exceeds the example with no additive. The behavior is indicative of an induction period. As seen in Fig. 6, TBAB has little effect on hydroformylation activity in water.

Table 1
Representative results for the hydroformylation of 1-octene

Solvent	Time	A/TPPTS ratio	Conversion (%)	Nonanal (%)	2-Me-octanal (%)	*n*/*iso* Ratio	Octane (%)	2-Octene (%)	Other[a] (%)
Water	24 h	0	35.3	82.5	7.6	10.9	0	6.0	3.9
Water	12 h	3	40.7	69.1	16.3	4.2	0.1	9.1	4.5
MeOH/water	45 min	0	42.1	49.7	13.4	3.7	1.8	23.2	11.9
MeOH/water	20 min	3	90.6	42.7	15.3	2.8	3.5	26.1	12.4
MeOH/water	20 min	15	42.4	30.5	16.6	1.8	2.5	34.5	15.9
EtOH/water	20 min	0	53.5	61.6	18.0	3.4	0.6	12.7	7.1
EtOH/water	20 min	3	84.2	38.5	14.7	2.6	4.0	28.3	14.5
EtOH/water	20 min	15	29.0	35.1	14.5	2.4	20.5	21.2	8.8

In the reactor 1.0 ml of catalyst solution was stirred for 1 h with CO/H_2 gas at 15 bar (220 psig) and 120 °C, [Rh] = 5.0 mM and [TPPTS] = 46.8 mM (P/Rh ratio = 9.4).

[a] Including alcohols.

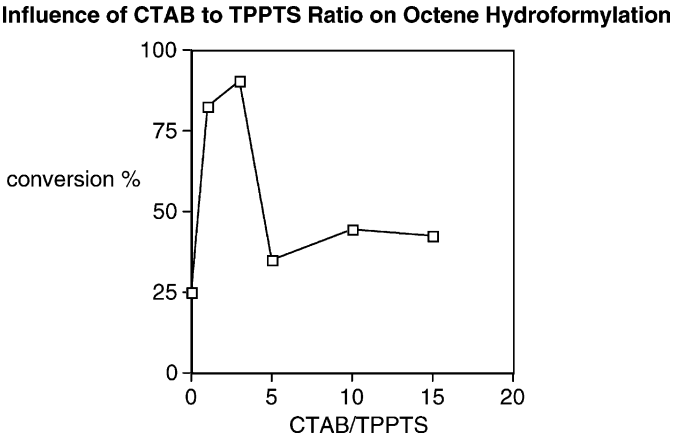

Fig. 2. The influence of CTAB on octene hydroformylation in aqueous methanol. TPPTS/Rh = 9.4; [Rh] = 5.0 mM; octene/Rh = 956; time = 20 min.

3.2. NMR studies and light scattering

The TPPTS/CTAB system was studied by ^{31}P NMR to see whether there are specific interactions between the tri-anionic TPPTS phosphine and the cationic surfactant, CTAB. These studies were done at CTAB concentrations that exceed its critical micelle concentration. The TPPTS chemical shift is strongly influenced by the presence of CTAB up to a ratio of CTAB/TPPTS of 3/1 (Fig. 7). At higher concentrations of CTAB, there is almost no additional change in chemical shift. At a ratio of CTAB/TPPTS of 10 and greater however a second TPPTS signal, at −5.05 ppm, is observed. This signal accounts for up to 75% of the total phosphine in the system. The relative intensity of the two signals goes through a maximum at a CTAB/TPPTS ratio of 20.

Addition of the non-amphiphilic quaternary ammonium ion, TBAB also shifts the TPPTS signal. The behavior is different than that observed with CTAB. Up to a ratio of TBAB/TPPTS of 3 there is almost no change in chemical shift while at higher ratios the signal moves upfield. This is the opposite trend compared to CTAB.

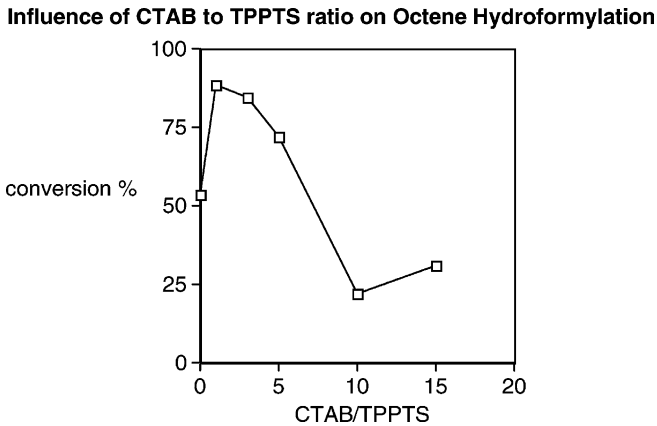

Fig. 3. The influence of CTAB on octene hydroformylation in aqueous ethanol. TPPTS/Rh = 9.4; [Rh] = 5.0 mM; octene/Rh = 956; time = 20 min.

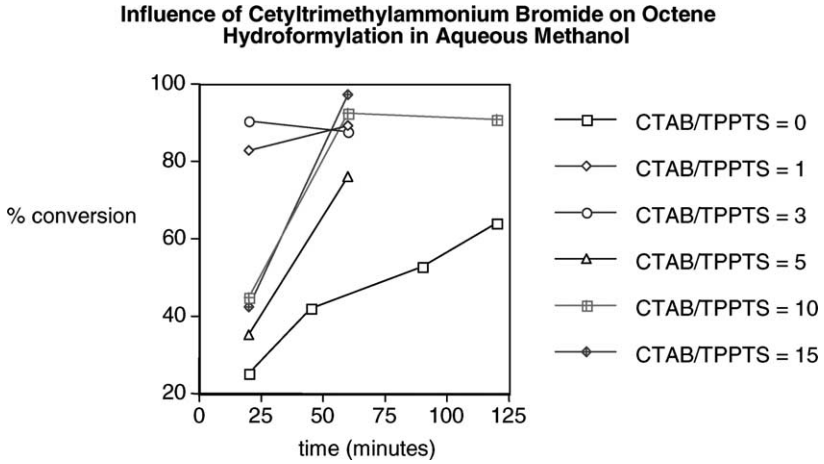

Fig. 4. The influence of CTAB on octene hydroformylation in aqueous methanol as a function of time. TPPTS/Rh = 9.4; [Rh] = 5.0 mM; octene/Rh = 956.

The chemical shift of phosphines is dictated in part by the steric size of the ligand [16]. Thus, one contributing factor in the chemical shift changes observed with the quaternary ammonium ions may be the conformation of the TPPTS ligand. The observed trend is that downfield chemical shifts are associated with larger cone angles. This is the opposite of what is expected for strong interaction with a micelle surface. That is, if all three sulfonate groups interact with the surface of a micelle then the cone angle for TPPTS is expected to be smaller than if the sulfonate groups are allowed to move as far apart as possible. Nonetheless, the NMR evidence suggests that the interaction of TPPTS with cationic micelles has a stoichiometry of three surfactant molecules to one TPPTS consistent with the ionic charges. The observation of a second TPPTS signal suggests two modes of binding of TPPTS to CTAB aggregates in solution. In aqueous methanol, the variation of chemical shift with CTAB concentration is similar to the behavior

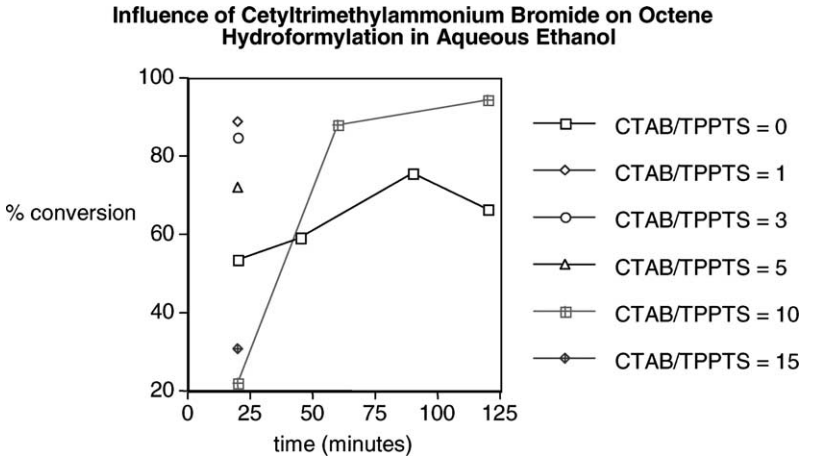

Fig. 5. The influence of CTAB on octene hydroformylation in aqueous ethanol as a function of time. TPPTS/Rh = 9.4; [Rh] = 5.0 mM; octene/Rh = 956.

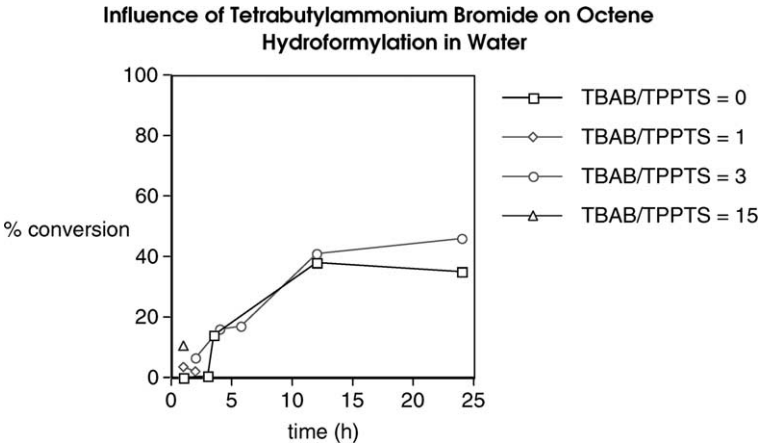

Fig. 6. The influence of TBAB on octene hydroformylation in aqueous methanol as a function of time. TPPTS/Rh = 9.4; [Rh] = 5.0 mM; octene/Rh = 956.

of the TBAB/TPPTS system in water. Thus, the interaction of CTAB and TPPTS in aqueous methanol is nonspecific and the direction of the chemical shift change upon adding CTAB is upfield.

It was thought that if TPPTS binds strongly to micelles then its diffusion rate in solution would be significantly slower in solutions that contain micelles than in solutions of pure TPPTS. PFG experiments were conducted to measure diffusion rates of TPPTS with and without added CTAB. These were measured to be 0.47×10^{-10} and $0.67 \times 10^{-10}\,m^2\,s^{-1}$, respectively. The similar rates suggest species of similar size moving through the solution. Thus, the micelle only marginally retards the movement of the TPPTS counterion. Micelles of course are dynamic and diffusion rates of small molecule surfactants are typically much greater than that of micelles themselves, so it is not surprising that TPPTS bound to the micelles should continue to move rapidly through solution. Diffusion rates were in the range 5.0×10^{-10} to

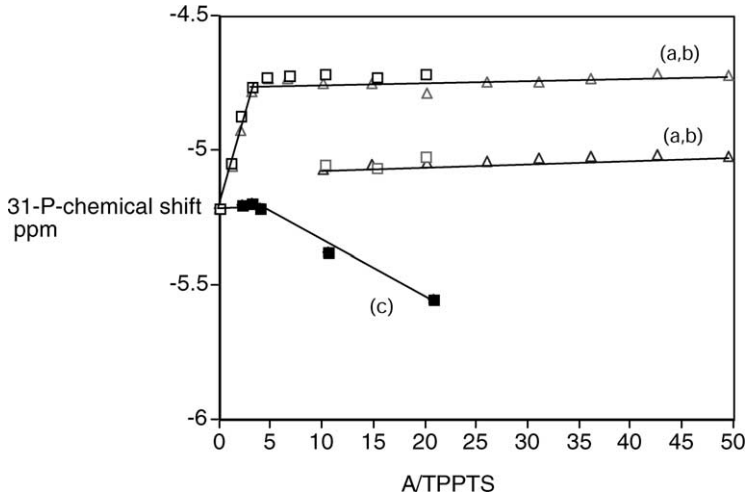

Fig. 7. (a and b) TPPTS chemical shifts as a function of CTAB/TPPTS ratio at concentrations of (△) 3.34 mM and (□) 4.68 mM in TPPTS; (c) TPPTS chemical shifts as a function of TBAB/TPPTS ratio at a TPPTS concentration of (■) 4.68 mM.

$9.0 \times 10^{-10}\,m^2\,s^{-1}$ when the measurements were done in aqueous methanol. A more complete study of diffusion rates at a variety of TPPTS and CTAB concentrations is needed to elucidate the role of micelle formation on TPPTS diffusion.

Dynamic light scattering studies were also carried out on the TPPTS/CTAB solutions. A consistent picture of micellar size was not obtained from these studies. The results were best modeled with a bimodal distribution of sizes with one component of dynamic radius of 100 Å and a second larger component of 300–400 Å. Both are significantly larger than observed for micelles of pure CTAB which have hydrodynamic radii of approximately 38 Å [17].

4. Conclusions

The addition of CTAB to biphasic hydroformylation catalysts has been suggested as a means to improve reaction activity while retaining selectivity to linear aldehydes [2–7]. Clearly the CTAB/TPPTS/rhodium catalyst system is very complicated. Under the reaction conditions used in this study, the hydroformylation selectivity suggests that the active rhodium catalyst bears just a single TPPTS ligand.

The observation of extremely large aggregates in solution and two TPPTS signals in the NMR spectrum at high CTAB concentrations suggests that vesicles may be formed in these systems. At high CTAB concentrations the advantage of improved activity is diminished and the hydroformylation selectivity is lost. In water, this is probably due to the strong interaction of TPPTS and CTAB micelles. Alternatively the lower activity may be due in part to the inaccessibility of the rhodium at high concentration of CTAB if vesicles are formed. The influence of CTAB on reaction activity in aqueous alcohol solvents may also be due to an interaction of CTAB and TPPTS however this is not reflected in the ^{31}P NMR chemical shift of TPPTS.

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