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Solubility Isotherms for $Cu(O_2CR)_2$ + Pyridine + Water Systems ($R = CH_3, C_2H_5$)

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Solubility isotherms measured for $Cu(O_2CR)_2$ + pyridine + water systems (298.2 K; $R = CH_3, C_2H_5$), conductivities, and electronic spectra show that R does not influence in an appreciable way the solute–water interactions, while R strongly influences the solubility of the $Cu_2(O_2CR)_4Py_2$ complexes in nonpolar media, particularly in aromatic solvents.

Introduction

Our previous results on the solubility and coordination equilibria in $Cu(O_2CR)_2$ ($R = CH_3$ and C_2H_5) + pyridine + chlorobenzene systems (*1*) have shown a striking difference between the solubility of copper(II) propionate and copper(II) acetate complexes with pyridine (Py) in chlorobenzene (0.9 and 0.22 × 10^{-2} mol dm^{-3}, per Cu atom, respectively). This difference diminishes in pyridine solutions (0.45 and 0.498 × 10^{-1} mol dm^{-3}) though still the ratio of the solubilities is about 10. As this difference decreases with increasing polarity of the medium, we have now investigated the solubility of the two copper(II) carboxylate complexes in a two-component solvent of increasing polarity: pyridine + water. No experimental data for such systems could be found in the literature.

Experimental Section

The binuclear complexes $Cu_2(O_2CR)_4Py_2$ were prepared by dissolving solid $Cu_2(O_2CR)_4(H_2O)_2$ in pure pyridine at about 310 K. The green products were precipitated by adding an excess of *n*-hexane and subsequent cooling to 270 K. The products were dried over anhydrous H_2SO_4 under reduced pressure and stored in a dessicator. They are quite stable in air. Anal. Found for $R = CH_3$: Cu, 24.2; Py, 30.1. Calcd: Cu, 24.38; Py, 30.33. Found for $R = C_2H_5$: Cu, 21.9; Py, 27.5. Calcd: Cu, 22.01; Py, 27.39. Mononuclear $Cu(O_2CR)_2Py_3$ were obtained by dissolution of binuclear $Cu_2(O_2CR)_4Py_2$ in hot dry pyridine (about 310 K) and cooling to 265 K. This procedure eliminates the formation of the hydrated $Cu(O_2CR)_2Py_3H_2O$ form, which is obtained by dissolution of $Cu_2(O_2CR)_4(H_2O)_2$ in hot pyridine. The dark blue crystals were stored over pure pyridine in a dessicator because they rapidly decompose in air, yielding binuclear complexes $Cu_2(O_2CR)_4Py_2$. Anal. Found for $R = CH_3$: Cu, 15.0; Py, 56.8. Calcd: Cu, 15.17; Py, 56.64. Found for $R = C_2H_5$: Cu, 14.1; Py, 53.2. Calcd: Cu, 14.22; Py, 53.08.

Solvents. Pyridine (POCH, pure) was dried by standing over KOH pellets and molecular sieves (4A) and rectified on a 30-plate column. Water was redistilled immediately before use.

Solubility measurements were performed by the column method (*2*) at (298.2 ± 0.2) K and checked by a static method (solutions saturated at about 305 K and allowed to equilibrate in a constant-temperature bath for several days, with occasional shaking).

Solutions were saturated with the solid phase in equilibrium, obtained in preliminary measurements. The solid phase in equilibrium with the saturated solutions was analyzed for Cu and Py. In the analysis for Cu, the weighted samples were shaken with water and titrated with EDTA by standard procedures; in the analysis for pyridine, the samples were dissolved in water acidified with HCl and the absorbancy at 255.5 nm was measured. The stoichiometry of the solid phases in equilibrium with the saturated solutions agreed with those indicated in Figure 1 within 2%. The data presented in Table I are mean values of at least three measurements; the reproducibility was within 3%.

Table I. Solubility of $Cu(O_2CR)_2$ in Pyridine + Water Mixtures at 298.2 K

X_{H_2O}	$s \times 10^2$/(mol dm^{-3})	X_{H_2O}	$s \times 10^2$/(mol dm^{-3})	X_{H_2O}	$s \times 10^2$/(mol dm^{-3})
		$R = CH_3$			
0	4.98	0.51	33.8	0.85	89.9
0.02	4.6	0.60	56.6	0.90	84.8
0.10	6.0	0.65	71.5	0.95	63.1
0.20	8.2	0.70	83.0	0.98	45.3
0.31	11.9	0.76	87.8	0.99	43.5
0.42	22.4	0.80	89.3		
		$R = C_2H_5$			
0	45.0	0.41	74.5	0.85	112.0
0.02	44.1	0.51	83.9	0.90	106.8
0.10	52.5	0.62	96.3	0.95	76.5
0.19	57.5	0.71	103.5	0.98	52.5
0.25	62.5	0.80	109.5	0.99	46.0
0.30	67.5				

Results and Discussion

Figure 1 represents the measured solubilities of $Cu(O_2CR)_2$ ($R = CH_3, C_2H_5$) in mixed pyridine + water solvent together with the stoichiometry of the solid phase in equilibrium. The solid phase in equilibrium with the pure pyridine solution is blue mononuclear $Cu(O_2CR)_2Py_3$. However small amounts of water in the mixed solvent ($X_{H_2O} \simeq 0.02$) result in precipitation of a blue product, $Cu(O_2CR)_2Py_3H_2O$. At $X_{H_2O} > 0.7$ the solid phase for $R = CH_3$ is blue $Cu(O_2CR)_2Py(H_2O)_4$. All three compounds are extremely unstable in air, loosing H_2O and the excess of pyridine to yield green ($R = CH_3$) or light green ($R = C_2H_5$) binuclear $Cu_2(O_2CR)_4Py_2$ (*3*). Except for $Cu(O_2CCH_3)Py_3$ (*4*) and $Cu(O_2CCH_3)_2Py_3H_2O$ (*5*) the blue complexes $Cu(O_2CR)_2Py_l(H_2O)_n$ mentioned above ($R = CH_3$: $l = 2$, $n = 4$. $R = C_2H_5$: $l = 3$, $n = 0$; $l = 3$, $n = 1$) have not been reported in the literature. Even in pure pyridine we could not obtain solid $Cu(O_2CCH_3)_2Py_4$ reported in ref 6.

The spectra of the $Cu(O_2CR)_2$ + pyridine + diluent systems indicate (*1*) that there are two equilibria in pure pyridine:

$$\underset{\text{mononuclear}}{2Cu(O_2CR)_2Py_2} \overset{K_b}{\rightleftharpoons} \underset{\text{binuclear}}{Cu_2(O_2CR)_4Py_2} + 2Py \qquad (1)$$

$$\underset{\text{mononuclear}}{Cu(O_2CR)_2Py_2} + Py \overset{K_m}{\rightleftharpoons} \underset{\text{mononuclear}}{Cu(O_2CR)_2Py_3} \qquad (2)$$

For acetate complexes, equilibrium 1 can be neglected [$K_b \simeq 0.8$ (*1*)]; however, for propionate complexes, the high solubility of copper(II) propionate results in an appreciable concentration of the binuclear complexes in the saturated pyridine solution (about 6.6%), in spite of the low K_b value [$K_b \simeq 0.8$ (*1*)]. The binuclear complexes dissociate into mononuclear compounds with increasing water concentration.

The complexes in pure pyridine and in solutions up to $X_{H_2O} \simeq 0.17$ are practically nonionic (at $c_{Cu} = 5 \times 10^{-3}$ mol dm^{-3}, the molar conductivities are 0.6 and 0.7 cm^2 Ω^{-1} equiv^{-1} for R

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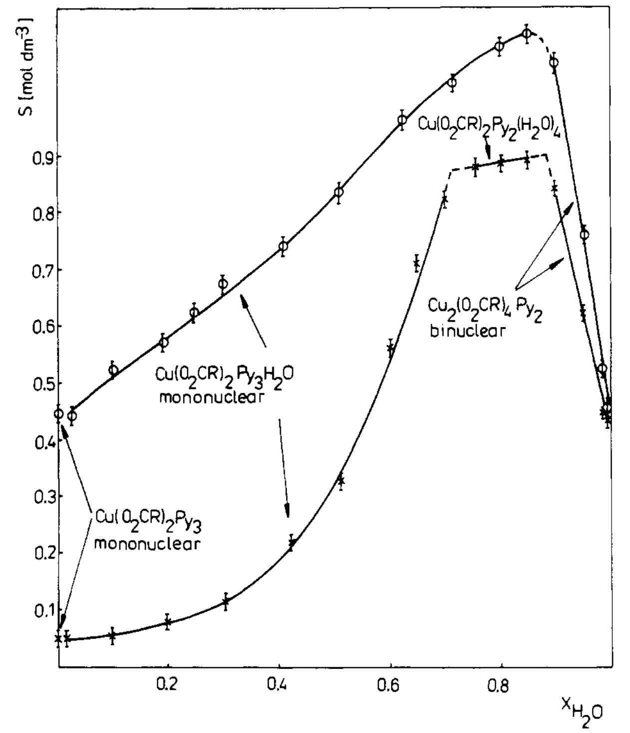

Figure 1. Solubility isotherms for $Cu(O_2CR)_2$ + pyridine + water systems, at 298.2 K: R = CH_3 (X); R = C_2H_5 (O). Solid phase in equilibrium with the saturated solutions indicated; *s* calculated per Cu atom.

= C_2H_5 and R = CH_3, respectively). At further dilution of the pyridine solutions with water, a gradual electrolytic dissociation and replacement of the pyridine molecules by water ligands occur. As could be expected, both processes are accompanied by an increase in solubility. For R = C_2H_5 the concentration of the saturated solutions increases up to $X_{H_2O} \simeq 0.9$, while for R = CH_3 there is a region of nearly constant solubility between $X_{H_2O} \simeq 0.7$ and 0.9. Above $X_{H_2O} \simeq 0.9$ the saturation curves of both systems drop very rapidly to the common value of $\simeq$0.45 mol dm^{-3} at $X_{H_2O} \simeq 1$. Now the solid phase becomes binuclear complex $Cu_2(O_2CR)_4Py_2$, retaining the pyridine molecules even at as low a pyridine content as X_{H_2O} = 0.99. The electronic spectra of the solutions saturated with the binuclear $Cu_2(O_2CR)_4Py_2$ correspond to mononuclear complexes only. The electronic spectra, solubilities, and conductivities of the two systems (R = CH_3 and C_2H_5) at pyridine concentrations approaching X_{H_2O} = 1 are very similar to each other, which suggests that the additional CH_2 group in the carboxylic ligand does not appreciably influence the solute-water interactions; at X_{H_2O} = 0.98 the mean molar absorptivity coefficients are 65 ± 3 at λ_{max} = 610 nm, and the conductivities at X_{H_2O} = 0.8 are 24 and 21 cm^2 Ω^{-1} equiv^{-1}, respectively. However this is not the case with the solute-nonpolar solvent interactions because the solubilities of two binuclear $Cu_2(O_2CR)_4Py_2$ in *n*-hexane and cyclohexane differ noticeably: they are 10^{-3} and 2×10^{-3} mol dm^{-3} for R = C_2H_5 and of the order of 10^{-4} mol dm^{-3} for R = CH_3. This difference is particularly great for aromatic solvents: 0.95 and 0.90 mol dm^{-3} for R = C_2H_5 in benzene and chlorobenzene and about 2×10^{-3} mol dm^3 in the two solvents for R = CH_3. Our attempts to obtain reliable (errors below 5%) solubility isotherms for analogous $Cu(O_2CR)_2$ complexes with longer hydrophobic chains (R > C_2H_5) were unsuccessful because of supersaturation effects. These effects increase rapidly with the length of R and make it difficult to obtain a real thermodynamic equilibrium between solid $Cu(O_2CR)_2Py_3H_2O$ and its saturated solutions. The results of the measurements for R > C_2H_5 are too poor to be a basis for any reliable interpretation.

Registry No. $Cu(O_2CCH_3)_2$, 142-71-2; $Cu(O_2CC_2H_5)_2$, 3112-74-1; pyridine, 110-86-1; $Cu(O_2CCH_3)_2Py_2$, 82872-28-4; $Cu(O_2CC_2H_5)_2Py_2$, 105033-58-7.

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The *N*,*N*-Dimethylformamide/Ethane-1,2-diol Solvent System. Density, Viscosity, and Excess Molar Volume at Various Temperatures

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Density (ρ), kinematic viscosity (ν), and absolute viscosity (η) are presented for mixtures of ethane-1,2-diol and *N*,*N*-dimethylformamide from -10 to +80 °C. The above properties were fitted by empirical equations stating their dependence on temperature and mole fraction of the mixture. Furthermore, some considerations regarding the meaning of the obtained adjustment parameters are made. The excess functions, such as molar volumes V^E, have been derived. The trends of V^E data vs mole fraction of the mixtures have exhibited markedly negative deviations from ideality, indicating extensive molecular interactions between the components of the binary solvent system.

Introduction

Among the most characterizing intensive chemical-physical properties of the solvent systems, density (ρ) and viscosity, either kinematic (ν) or dynamic (η), represent some of the common thermomechanical parameters that are in general useful in order to study and interpret the medium effects on the transport phenomena, on the electrolyte behavior, and on any other reaction mechanism that takes place in solution. In particular, in the field of conductometric studies, it's impossible to approach any problem without the preliminary knowledge of the above-mentioned solvent properties. In fact, if one thinks about the phenomena of electrolyte diffusion and electropho-

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