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THE ENTHALPIES OF SOLUTION OF TETRAPHENYLSILANE IN PYRIDINE–OTHER SOLVENT MIXTURES

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ABSTRACT

Enthalpies of solution and the corresponding enthalpies of transfer from pyridine to its mixtures with other solvents are reported for tetraphenylsilane ($SiPh_4$) at 298.15 K. For some systems, the free energies and entropies of transfer of the solute have also been determined.

INTRODUCTION

In preceding papers we discussed the solute–solvent interactions of $NiCl_2py_4$ [1,2] and other similar complexes involving pyridine as the neutral ligand [3–5]. We have found that the complex may interact specifically with non-coordinating protic solvents such as chloroform as well as with weakly basic donor solvents. Similar conclusions about the interactions with protic solvents have been drawn earlier by Narbutt and Siekierski, who studied the complex $Co(NCS)_2(\gamma\text{-pic})_4$ [6]. However, the controversial question has arisen as to whether the $d \rightarrow \pi^*$ electron delocalization from the central metal atom to the amine-ligands in these complexes is important and whether it significantly affects their outer-sphere interactions with the solvent. It seemed that comparison of solvation behaviour of complexes of the MX_2py_4 type with that of tetraphenylsilane ($SiPh_4$) should be helpful in solving this problem because $SiPh_4$ is a solute possessing π-electrons in its four aromatic rings but without d_π electrons available for delocalization. In this paper we report the enthalpic solvation characteristics of $SiPh_4$ in binary mixtures of pyridine with a number of various diluents. Pyridine, a coordinating solvent used in investigations of halogenopyridinate metal complexes was necessary to maintain the required stoichiometry (MX_2py_4) of the metal complexes in solutions. For the pyridine + chloroform and

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pyridine + chlorobenzene systems (solvents especially important for our research program of metal complexes) the free energies and entropies of transfer of $SiPh_4$ from pyridine to pyridine + diluent mixtures of variable composition have also been determined.

EXPERIMENTAL

The solvents were purified and dried by standard methods [7] and finally fractionally distilled.

Tetraphenylsilane was kindly supplied by Organosilane Compounds Laboratory of the Institute of Inorganic Chemistry and Technology. It was obtained by Grignard reaction: dichlorophenylsilane ($PhSiCl_2$) was added to phenylmagnesium bromide (PhMgBr) (prepared from PhBr and Mg) in anhydrous THF (tetrahydrofuran). The whole mixture was heated for several hours under reflux. Toluene was then added and the mixture was hydrolyzed with water acidified with HCl. The organic layer was washed out with water and dried with anhydrous $MgSO_4$. Solvents were removed by evaporation and the residue was crystallized twice from toluene. Melting point of the $SiPh_4$ was 511 K.

Heats of solution of tetraphenylsilane in pyridine + diluent mixtures of variable composition were determined by using the reaction calorimeter described elsewhere [8]. It consists of a 100 cm^3 glass vessel and a 1 cm^3 teflon ampoule with a thin-glass bottom which was crushed to start the reaction. The glass vessel was contained inside a metal can submerged in a thermostat bath kept at 298.15 ± 0.003 K. The temperature was measured with a 47 kΩ thermistor $\pm 5 \times 10^{-5}$ K. The heat capacity of the calorimetric system was determined electrically with an accuracy of ± 0.2% over the total temperature range of 0.1 K.

Solubilities were determined by using the saturating column method [9] and concentration of $SiPh_4$ was determined by drying weighed amounts of the solution and weighing the residue. ΔG^0_{tr} values have also been calculated [2].

RESULTS AND DISCUSSION

Solubilities and heats of solution of $SiPh_4$ in pyridine + chloroform and pyridine + chlorobenzene systems, and the derived standard transfer functions are listed in Table 1. Plots of the functions for pyridine + chloroform mixtures are shown in Fig. 1. The respective values for pyridine + chlorobenzene system are close to zero over the whole pyridine mole fraction range. The heats of solution and enthalpies of transfer of $SiPh_4$ for pyridine + diluent mixtures are given in Table 2 for the diluents: cyclohexane, ethyl

TABLE 1

Solubilities (s) and heats of solution (ΔH_s) of tetraphenylsilane in pyridine + diluent mixtures at 298.15 K and the derived standard free energies (ΔG^0_{tr}), enthalpies (ΔH^0_{tr}) and entropies (ΔS^0_{tr}) [a] of transfer of the solute from pyridine to pyridine + diluent mixtures (x_{py} = mole fraction of pyridine)

x_{py}	$10^2 \times s$ (mol dm^{-3})	ΔG^0_{tr} (kJ mol^{-1})	x_{py}	ΔH_s (kJ mol^{-1})	ΔH^0_{tr} (kJ mol^{-1})	$\Delta S^{0\,a}_{tr}$ (J K^{-1} mol^{-1})
1	6.36	0	1	25.94 ± 0.09	0	0
Pyridine + chlorobenzene						
0.746	6.10		0.862	25.59	−0.4	
0.500	6.32	0 ± 0.1	0.749	26.18	0.2	−0.2 ± 0.5
0.239	6.37		0.606	25.25	−0.7	
0	6.48		0.496	25.48	−0.5	
			0.378	26.14	0.2	
			0.271	25.88	−0.1	
Pyridine + chloroform						
0.804	5.49	0.37	0.810	27.58	1.6	4.3
0.606	5.32	0.44	0.595	28.71	2.8	7.9
0.412	5.77	0.24	0.491	29.00	3.1	9.1
0.214	7.30	−0.34	0.294	27.93	2.0	6.8
0.020	12.21	−1.62	0.159	26.78	0.8	4.9
			0.050	25.51	−0.4	3.1
			0.002	25.03	−0.9	2.6

[a] Calculated using interpolated values of ΔG^0_{tr}.

acetate, dioxane, benzene, toluene, carbon tetrachloride, and aniline. Respective plots of the ΔH^0_{tr} vs. pyridine mole fraction are shown in Figs. 2 and 3.

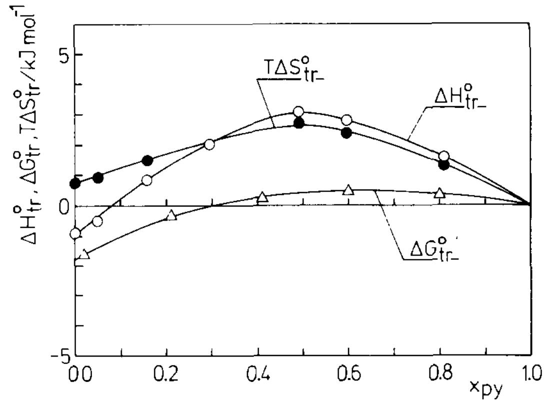

Fig. 1. Plots of the transfer functions ΔG^0_{tr}, ΔH^0_{tr} and $T\Delta S^0_{tr}$ of tetraphenylsilane from pyridine to pyridine + chloroform mixtures vs. pyridine mole fraction (x_{py}), at 298.15 K.

TABLE 2

Heats of solution (ΔH_s) and enthalpies of transfer (ΔH_{tr}^0) of tetraphenylsilane from pyridine to pyridine + diluent mixtures, at 298.15 K (x_{py} = mole fraction of pyridine)

x_{py}	ΔH_s (kJ mol^{-1})	ΔH_{tr}^0 (kJ mol^{-1})	x_{py}	ΔH_s (kJ mol^{-1})	ΔH_{tr}^0 (kJ mol^{-1})
Pyridine + benzene			*Pyridine + ethyl acetate*		
0.812	26.11	0.2	0.706	26.38	0.4
0.610	25.29	−0.7	0.492	27.00	1.1
0.427	24.83	−1.1	0.200	27.08	1.1
0.279	24.48	−1.5	0.035	26.97	1.0
0.134	24.22	−1.7	0	30.88	4.9
0	23.47	−2.5			
			Pyridine + carbon tetrachloride		
Pyridine + toluene			0.784	26.43	0.5
0.764	25.46	−0.5	0.544	25.56	−0.4
0.589	25.56	−0.4	0.372	25.45	−0.5
0.286	25.37	−0.6	0.200	24.27	−1.7
0.139	25.07	−0.9	0.164	24.27	−1.7
0	24.71	−1.2	0	24.53	−1.4
Pyridine + dioxane			*Pyridine + cyclohexane*		
0.788	25.92	0	0.832	26.73	0.8
0.616	25.95	0	0.734	26.58	0.6
0.408	26.11	0.2	0.570	27.37	1.4
0.222	26.10	0.2	0.333	27.92	2.0
0	26.39	0.5	0.142	28.77	2.8
			0.077	29.08	3.1
Pyridine + aniline			0.038	29.76	3.8
0.765	26.08	0.1	0	35.96	10.0
0.525	29.07	3.1			
0.263	29.56	3.6			
0	31.80	5.9			

Generally, the differences in the enthalpies of transfer of $SiPh_4$ from pyridine to various pure diluents are small which suggests the presence of weakly polar bonds in the solute molecule. The difference of electronegativity between silane and carbon atom (1.8 and 2.5, respectively on Pauling scale) indicate that the polarization of phenyl C–H bonds in $SiPh_4$ is weak. It seems that most of the SiPh–solvent interactions are due to dispersion and quadrupole interactions, only partly modified by weak donor–acceptor interactions: π–π type (aromatic solvents), $\pi_{phenyl} \rightarrow \sigma$ * type [10,11] (solvents with acceptor orbitals of σ type, such as carbon tetrachloride and chloroform), and n-π_{phenyl} type (10) (solvents with a nonbonding electron pair). The ΔH_{tr}^0 data obtained show that dipole–induced dipole type interactions are not significant in tetraphenylsilane solvation.

A relatively high positive value of ΔH_{tr}^0 of $SiPh_4$ from pyridine to aniline (4.9 kJ mol^{-1}) may be explained by strong association of the diluent [12]; an

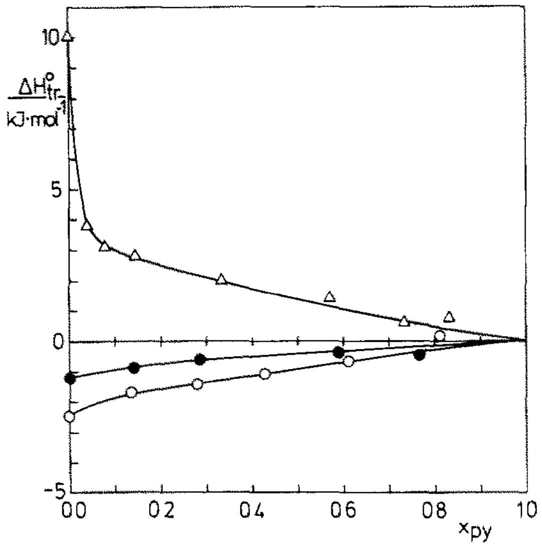

Fig. 2. Plots of the enthalpies of transfer ΔH^0_{tr} of tetraphenylsilane from pyridine to pyridine + cyclohexane (△), pyridine + toluene (●), and pyridine + benzene (⊙) mixtures vs. pyridine mole fraction (x_{py}), at 298.15 K.

energetic contribution is needed for reorganisation of solvent structure when the solute molecules are dissolved within it. The free energies and enthalpies of transfer of $SiPh_4$ for the pyridine + chlorobenzene system are close to zero in the whole mole fraction range; consequently, the values for entropy of transfer are close to zero also.

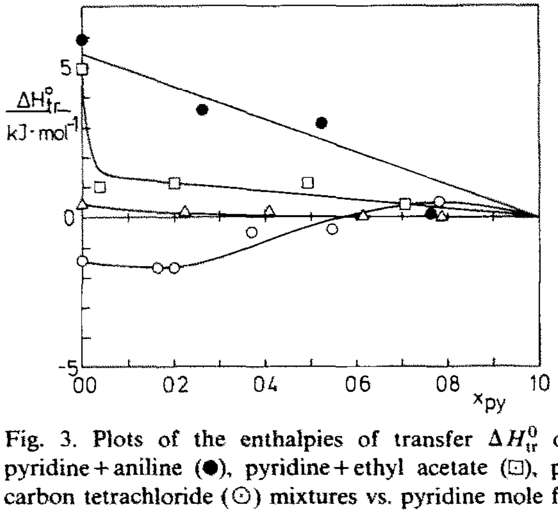

Fig. 3. Plots of the enthalpies of transfer ΔH^0_{tr} of tetraphenylsilane from pyridine to pyridine + aniline (●), pyridine + ethyl acetate (□), pyridine + dioxane (△), and pyridine + carbon tetrachloride (⊙) mixtures vs. pyridine mole fraction (x_{py}), at 298.15 K.

Plots of the enthalpy of transfer against the pyridine mole fraction for pyridine–cyclohexane (Fig. 2) and pyridine + ethyl acetate (Fig. 3) mixtures suggest preferential solvation of $SiPh_4$ by pyridine molecules. For the first system, data for the enthalpy of mixing of pyridine with cyclohexane [13] together with our data for the enthalpy of transfer of $SiPh_4$, interpreted in terms of the theory of solvation given by Waghorne et al. [14] and Cox et al. [15], support this qualitative supposition (a linear relationship of ΔH_{tr}^0 vs. relative partial molal enthalpy of pyridine was obtained for most pyridine + cyclohexane mixed solvent compositions). This theory was also helpful in determining the type of solvation of $SiPh_4$ for mixtures of pyridine + toluene and pyridine + carbon tetrachloride (over the whole range of solvent composition), as well as for pyridine + chloroform mixtures (in the range $0.4 < x_{py} < 1$); data for enthalpy of mixing of mixtures of pyridine + toluene, pyridine + CCl_4 and pyridine + chloroform were taken from refs. 16 and 17 and 18, respectively. The linear relationships, for these mixed solvents, suggest a random solvation of $SiPh_4$ (relationship of $\Delta H_{tr}^0/x_D$ and $\Delta H^E/x_D$; ΔH^E = enthalpy of mixing, x_D = mole fraction of the diluent). In such a case composition of the solvation sphere of the solute is the same as that of the bulk solvent. For the other solvent mixtures investigated (pyridine + benzene, pyridine + dioxane, pyridine + aniline; heats of mixing from refs. 13, 19 and 20, respectively) the theory of solvation [14,15] fails, probably because its assumptions are not satisfied by the systems under study. The variation of enthalpy of transfer of $SiPh_4$ with the pyridine mole fraction for binary mixtures of pyridine with carbon tetrachloride (Fig. 3) and chloroform (Fig. 1) show an endothermic maximum. Similar maxima appear on the profiles of the heats of mixing of the binary solvents, suggesting formation of relatively strong molecular complexes. The presence of such complexes, e.g. $py \cdot CCl_4$ [21–23] and $py \cdot CHCl_3$ [24–26], has been widely discussed. According to the model of Cox and Waghorne [14,15], which has assumed compensation of the enthalpic and entropic contributions from the solvent–solvent interactions, the ΔG_{tr}^0 values essentially reflect the interactions between the solute and solvent molecules in the solvation shell. The values of ΔG_{tr}^0 of $SiPh_4$ for the pyridine + chloroform system are close to zero over the mole fraction range $0.2 < x_{py} < 1$. This suggests that the maximum of ΔH_{tr}^0 (Fig. 1) reflects the enhancement of the mixed-solvent structure in relation to pure pyridine.

Comparison of the enthalpies of transfer of $SiPh_4$ for pyridine + CCl_4 mixtures with those for pyridine + $CHCl_3$ indicates that acidic hydrogen in $CHCl_3$ molecules does not increase interaction energy of the solvent with $SiPh_4$, whereas its role in outer-sphere interactions with halogenopyridinate transition metal complexes is important [1–5].

Comparison of solvation behaviour of $SiPh_4$ with the electroneutral complexes of the MX_2py_n type will be presented later.

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