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CALORIMETRIC DETERMINATION OF LOG K_i, ΔH_i^0, AND ΔS_i^0 VALUES FOR THE INTERACTION OF THIOUREA WITH $Hg(CN)_2$ IN WATER–FORMAMIDE SOLVENTS AT 25°C*

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ABSTRACT

Log K_i, ΔH_i^0, and ΔS_i^0 ($i = 1, 2$) values have been determined calorimetrically at 25°C for the consecutive reaction of thiourea (Tu) with $Hg(CN)_2$ to form $Hg(CN)_2Tu_2$ in formamide–water solvents. The log K_i, ΔH_i^0, and ΔS_i^0 values determined in 20, 40, 60, 80, and 100% (w/w) formamide show little deviation from those which were determined previously in aqueous solution. The leveling nature of the formamide–water solvents is discussed and the results are compared with those obtained earlier in water and ethanol–water solvents.

INTRODUCTION

This paper is part of a continuing study dealing with the effects of solvent structure and dielectric constant (D) upon weak electrostatic interactions (*i.e.*, dipole–dipole and induced dipole–dipole). The $Hg(CN)_2$–thiourea (Tu) system is ideal for the investigation of these weak interactions since all interacting species are uncharged. In the earlier study[1] log K_i, ΔH_i^0 and ΔS_i^0 ($i = 1, 2$) values were reported for reactions (1) and (2) in ethanol–water solvents.

$$Hg(CN)_2 + Tu \rightleftharpoons Hg(CN)_2Tu \qquad (1)$$

$$Hg(CN)_2Tu + Tu \rightleftharpoons Hg(CN)_2Tu_2 \qquad (2)$$

In that study significant changes were found in the ΔH_i^0 and ΔS_i^0 values as the mole fraction of the non-aqueous solvent component was increased indicating the probable formation of solvent–solvent or solvent–solute complexes.

In the present investigation reactions (1) and (2) were studied calorimetrically in formamide–water mixtures. Because formamide ($D = 109.5$ (Ref. 2) at 25°C) has solvent properties which are similar[3-5] to those of water and because formamide–water solvents have a high solvation nature electrostatic effects are much less pro-

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nounced[6] than in media of lower dielectric constant such as the ethanol–water mixtures studied previously.

Very few calorimetric or other thermodynamic data have been reported for metal–ligand reactions in solvents having dielectric constants greater than that of water. Heats of solution[6] specific heats[7], and densities[7] of aqueous formamide solutions have been determined as have heats of solution and solvation for selected electrolytes in HF[8], anhydrous formamide[6,9], *N*-methylformamide[10], and *N*-methylacetamide[11]. In addition, standard cell potentials, entropies, and activity coefficients have been calculated*[,12,13] from electromotive force and conductance data. However, in none of these studies have ΔG, ΔH, or ΔS values been reported for metal–ligand interaction. Changes occurring in the log K, ΔH, and ΔS values for metal ligand interaction as the solvent composition is varied reflect changes in solvent–solute behavior and the determination of these values as a function of solvent composition should result in useful information regarding the nature of the solvent medium.

Log K_i, ΔH_i^0, and ΔS_i^0 ($i = 1, 2$) values are reported here for reactions (1) and (2) in 20, 60, 80, and 100% (w/w) formamide. Comparison is also made with the thermodynamic values valid in ethanol–water solvents which were reported previously[1].

EXPERIMENTAL

Materials

Reagent grade Tu (Baker 'Analyzed') and $Hg(CN)_2$ (Mallinckrodt) were used in the preparation of solutions. Reagent grade formamide (Baker) was decolorized with activated charcoal and purified just prior to use by 5 successive freezings using a procedure similar to that suggested by Dawson *et al.*[14]. Each freezing was carried out such that about 80% of a 1500–2000 ml portion was crystallized, and the remaining liquid was poured off. The purified formamide and formamide–water solvents and solutions were stored and used under an atmosphere of dry nitrogen. Boiled, doubly distilled water was used in the preparation of the formamide–water solvents.

Procedures and calculations

The calorimetric titration technique[15] and calorimetric equipment[16] have been described.

The calorimetric data were obtained by titrating 1.3*m* Tu into 0.025 and 0.04*m* $Hg(CN)_2$ solutions and were analyzed for log K_i and ΔH_i^0 values using procedures developed by us[17].

Values for the heat capacities and densities at 25° of 20, 40, 60, 80, and 100% (w/w) formamide were taken from the literature[7].

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*Ref. 5 contains a compilation of electromotive force, conductance, polarographic and cryoscopic studies carried out in amine solvents.

RESULTS

In Table I are given calorimetric heat of dilution data for thiourea (Tu) in water–formamide solvents. Sample calorimetric titration data for the $Hg(CN)_2$–thiourea system are given in Table II. In Table III are given additional data which can be combined with the data in Tables I and II to calculate for each solvent system log K, ΔH° and ΔS° values for the reaction

$$Hg(CN)_2 + i\text{Tu} = Hg(CN)_2\text{Tu}_i$$

where $i = 1, 2$.

TABLE I

HEAT OF DILUTION DATA FOR THIOUREA IN WATER–FORMAMIDE SOLVENTS

I	Q_c				
	Run 1	*Run 2*	*Run 3*	*Run 4*	*Run 5*
1	0.089	0.044	0.009	−0.012	−0.020
2	0.166	0.083	0.014	−0.020	−0.038
3	0.245	0.133	0.034	−0.025	−0.058
4	0.320	0.180	0.055	−0.028	−0.086
5	0.396	0.226	0.077	−0.043	−0.115
6	0.472	0.272	0.098	−0.032	−0.139
7	0.549	0.317	0.117	−0.037	0.156
8	0.621	0.362	0.138	−0.038	−0.183
9	0.695	0.407	0.158	−0.039	−0.204
10	0.769	0.450	0.179	−0.042	−0.220
11	0.843	0.492	0.200	−0.045	−0.241
12	0.914	0.532	0.222	−0.045	−0.261
13	0.994	0.575	0.244	−0.043	−0.280
14	1.068	0.619	0.266	−0.041	−0.300
15	1.141	0.662	0.289	−0.042	−0.319
16	1.214	0.705	0.311	−0.042	−0.335
17	1.287	0.746	0.333	−0.042	−0.352
18	1.362	0.787	0.356	−0.043	−0.376

Q_c (cal) values in Tables I and II are corrected for all heat effects (including those due to dilution of the titrant) except those due to reactions occuring in the calorimeter; $T = 25.0°$. The I value refers to the column heading "mmole of titrant at point I" in Table III (*i.e.*, for run 1, point 10, mmole of tritant $= 0.4437 \times 10 + 0.0721 = 4.509$). For all runs, initial volume $= 99.95$ ml.

The values of log K_i, ΔH_i^0, and ΔS_i^0 ($i = 1, 2$) for reactions (1) and (2) in formamide–water solvents are given in Table IV.

TABLE II

TYPICAL CALORIMETRIC TITRATION DATA FOR THE INTERACTION OF THIOUREA WITH $Hg(CN)_2$

I	Q_c									
	Run 6	*Run 7*	*Run 8*	*Run 9*	*Run 10*	*Run 11*	*Run 12*	*Run 13*	*Run 14*	*Run 15*
1	−0.3342	−0.4473	−0.3458	−0.4810	−0.3449	−0.4448	−0.3256	−0.4319	−0.3023	−0.3928
2	−0.5729	−0.7573	−0.6051	−0.8338	−0.6302	−0.7765	−0.5736	−0.7581	−0.5395	−0.7032
3	−0.8077	−1.0697	−0.8663	−1.1824	−0.8950	−1.1235	−0.8181	−1.0814	−0.7732	−1.0106
4	−1.0375	−1.3775	−1.1236	−1.5266	−1.1541	−1.4742	−1.0639	−1.4019	−1.0034	−1.2980
5	−1.2656	−1.6864	−1.3824	−1.8682	−1.4072	−1.8068	−1.3064	−1.7197	−1.2262	−1.5954
6	−1.4970	−1.9954	−1.6347	−2.2084	−1.6540	−2.1427	−1.5456	−2.0441	−1.4586	−1.8901
7	−1.7207	−2.3019	−1.8894	−2.5491	−1.9046	−2.4754	−1.7908	−2.3658	−1.6795	−2.1864
8	−1.9392	−2.6083	−2.1318	−2.8849	−2.1496	−2.7894	−2.0231	−2.4352	−1.8930	−2.4629
9	−2.1559	−2.9038	−2.3687	−3.2166	−2.3807	−3.2111	−2.2473	−2.9864	−2.1034	−2.7454
10	−2.3721	−3.1991	−2.6032	−3.5353	−2.6163	−3.4369	−2.4680	−3.2853	−2.3065	−3.0167
11	−2.5817	−3.4931	−2.8341	−3.8543	−2.8490	−3.7445	−2.6756	−3.5812	−2.5021	−3.2896
12	−2.7884	−3.7821	−3.0615	−4.1691	−3.0737	−4.0442	−2.8890	−3.8740	−2.6947	−3.5512
13	−2.9920	−4.0648	−3.2875	−4.4853	−3.2975	−4.3463	−3.1035	−4.1684	−2.8927	−3.8144
14	−3.1926	−4.3473	−3.5076	−4.7937	−3.5151	−4.6403	−3.3094	−4.4501	−3.0877	−4.0748
15	−3.3901	−4.6246	−3.7252	−5.0989	−3.7212	−4.9336	−3.5163	−4.7333	−3.2795	−4.3413
16	−3.5821	−4.8980	−3.9333	−5.3929	−3.9252	−5.2229	−3.7098	−5.0037	−3.4638	−4.6007
17	−3.7723	−5.1711	−4.1410	−5.6891	−4.1291	−5.5008	−3.8898	−5.2754	−3.6363	−4.8573
18	−3.9593	−5.4267	−4.3449	−5.9775	−4.3265	−5.7777	−4.0849	−5.5436	−3.8098	−5.0937
19	−4.1444	−5.7041	−4.5472	−6.2658	−4.5258	−6.0547	−4.2616	−5.8084	−3.9713	−5.3184
20	−4.3300	−5.9676	−4.7422	−6.5495	−4.7039	−6.3274	−4.4437	−6.0599	−4.1426	−5.5797
21	−4.5050	−6.2209	−4.9344	−6.8286	−4.8911	−6.5927	−4.6265	−6.3030	−4.3106	−5.8556
22	−4.6781	−6.4763	−5.1215	−7.0984	−5.0675	−6.8516	−4.8100	−6.5423	−4.4796	−6.0410
23	−4.8516	−6.7238	−5.3046	−7.3692	−5.2445	−7.1092	−4.9602	−6.7972	−4.6409	−6.2628
24	−5.0195	−6.9746	−5.4882	−7.6353	−5.4232	−7.3519	−5.1206	−7.0627	−4.7944	−6.4859
25	−5.1865	−7.2150	−5.6735	−7.9011	−5.5940	−7.6092	−5.2814	−7.3003	−4.9445	−6.7149
26	−5.3478	−7.4525	−5.8571	−8.1575	−5.7623	−7.8471	−5.4330	−7.5145	−5.0910	−6.9365
27	−5.5107	−7.6894	−6.0205	−8.4102	−5.9205	−8.0773	−5.6190	−7.7295	−5.2296	−7.1549
28	−5.6641	−7.9221	−6.1843	−8.6556	−6.0813	−8.3103	−5.7421	−7.9843	−5.3736	−7.3570
29	−5.8141	−8.1468	−6.3474	−8.8938	−6.2384	−8.5429	−5.8849	−8.2058	−5.5229	−7.5692
30	−5.9633	−8.3708	−6.5110	−9.1328	−6.3896	−8.7666	−6.0281	−8.4183	−5.6552	−7.7694
31	−6.1141	−8.5931	−6.6692	−9.3714	−6.5379	−8.9792	−6.1616	−8.6266	−5.7929	−7.9618
32	−6.2590	−8.8110	−6.8220	−9.6026	−6.6803	−9.1924	−6.3150	−8.8257	−5.9314	−8.1599
33	−6.4018	−9.0308	−6.9705	−9.8357	−6.8273	−9.4061	−6.4441	−9.0352	−6.0708	−8.3548
34	−6.5386	−9.2398	−7.1195	−10.0568	−6.9661	−9.6096	−6.5634	−9.2453	−6.1930	−8.5463
35	−6.6719	−9.4470	−7.2641	−10.2832	−7.1021	−9.8019	−6.6877	−9.4461	−6.3025	−8.7301
36	−6.8081	−9.6548	−7.4090	−10.5056	−7.2384	−10.0043	−6.8072	−9.6277		−8.9014

TABLE III

SUPPLEMENTARY DATA USED IN CONVERSION OF DATA IN TABLES I AND II TO LOG K AND ΔH^0 VALUES

Run	*Titrant Tu (m)*	*Solution in calorimeter*	*mmoles of titrant at point I*	*Solvent (wt % formamide)*
1	1.370	Solvent	$0.4437 \times I + 0.0721$	20.0
2	1.369	Solvent	$0.4536 \times I + 0.0657$	40.0
3	1.313	Solvent	$0.4461 \times I + 0.0568$	60.0
4	1.287	Solvent	$0.4469 \times I + 0.0670$	80.0
5	1.262	Solvent	$0.4478 \times I + 0.0559$	100.0
6	1.370	0.02522 m $Hg(CN)_2$	$0.2218 \times I + 0.0709$	20.0
7	1.370	0.03888 m $Hg(CN)_2$	$0.2218 \times I + 0.0798$	20.0
8	1.369	0.02476 m $Hg(CN)_2$	$0.2268 \times I + 0.0748$	40.0
9	1.369	0.03826 m $Hg(CN)_2$	$0.2268 \times I + 0.0646$	40.0
10	1.313	0.02425 m $Hg(CN)_2$	$0.2231 \times I + 0.0591$	60.0
11	1.313	0.03646 m $Hg(CN)_2$	$0.2231 \times I + 0.0684$	60.0
12	1.286	0.02370 m $Hg(CN)_2$	$0.2233 \times I + 0.0670$	80.0
13	1.286	0.03648 m $Hg(CN)_2$	$0.2233 \times I + 0.0647$	80.0
14	1.263	0.02298 m $Hg(CN)_2$	$0.2239 \times I + 0.0559$	100.0
15	1.263	0.03572 m $Hg(CN)_2$	$0.2239 \times I + 0.0618$	100.0

TABLE IV

LOG K_i, ΔH_i^0 AND ΔS_i^0 VALUES FOR THE STEPWISE INTERACTION OF Tu WITH $Hg(CN)_2$ IN FORMAMIDE–WATER SOLVENT MIXTURES AT 25°C AND $m = 0^a$

Formamide (%, w/w)	*Log K_1*	*Log K_2*	*ΔH_1^0 (kcal/gmole)*	*ΔH_2^0 (kcal/gmole)*	*ΔS_1^0 (cal·g^{-1}·degree^{-1})*	*ΔS_2^0 (cal·g^{-1}·degree^{-1})*
0	1.97 ± 0.06^b	0.58 ± 0.04^b	-1.5 ± 0.1^b	-7.9 ± 0.2^b	4.0^b	-23.8^b
20	2.08 ± 0.06	0.56 ± 0.10	-1.4 ± 0.1	-9.1 ± 0.4	4.8	−28
40	1.95 ± 0.05	0.57 ± 0.11	-1.7 ± 0.1	-9.2 ± 0.4	3.2	−28
60	2.01 ± 0.08	0.60 ± 0.09	-1.7 ± 0.1	-8.7 ± 0.4	3.5	−26
80	2.02 ± 0.08	0.64 ± 0.11	-1.6 ± 0.1	-7.8 ± 0.4	3.8	−23
100	2.02 ± 0.08	0.64 ± 0.11	-1.5 ± 0.1	-7.4 ± 0.4	4.0	−22

[a] The uncertainties are expressed as standard deviations among 8–24 runs for each solvent composition; the thermodynamic values are expressed in molal units based on densities and heat capacities taken from Ref. 8. [b] Ref. 1.

DISCUSSION

Examination of the thermodynamic values in Table IV reveals the striking fact that the values do not vary significantly as the ratio of formamide to water in the solvent is increased and in general the results show little deviation from those values determined in pure water. This leveling nature of formamide towards the thermodynamic quantities for the interaction of Tu with $Hg(CN)_2$ confirms previous views[3,4,6] that formamide is a water-like solvent.

Dawson and co-workers[3,4] consider the properties of formamide to be of interest because of their striking similarity to those of water. Somsen and Coops[6] have taken anhydrous formamide as an ideal solvent for determining enthalpies of solvation because (*a*) the use of other binary solvents may lead to a distorted picture because of preferential solvation[18–20] and (*b*) there appears to be little or no ion pairing in formamide solutions. Support for the idea that little or no ion pairing occurs in formamide solvents is found in the cryoscopic and conductometric measurements by Dawson *et al.*[3,4]. However, in a recent X-ray study of KI solutions in formamide, DeSando and Brown[21] present evidence for ion-pair formation at various concentrations. The possibility of the non-electrolyte, thiourea, dimerizing in formamide–water solvents is unlikely and freezing-point depression measurements in this laboratory indicate no Tu dimerization in 100% formamide.

In our earlier study[1] of $Hg(CN)_2$–Tu interaction in ethanol–water solvents the marked change of 2–5 kcal/mole in the ΔH^0 and $T\Delta S^0$ values in the 0–50% (w/w) ethanol region were taken to be indicative of changes in the solvent structure and for solute–solvent interactions. To investigate the possibility of similar types of changes for the formamide–water solvent system the thermodynamic data for reaction (1) were first re-evaluated on the mole fractions scale[22] and the recalculated values are given in Table V. These values indicate there is a decrease in the stability of the complex in comparing the ΔG^0 values for pure water to those for pure formamide. The decrease in $-\Delta G^0$ cannot be attributed solely to changes in the dipole interactions between $Hg(CN)_2$ and Tu as the dielectric constant decreases since the ΔH^0 values remain essentially unchanged. The decrease is more probably due to changes in solvation of the $Hg(CN)_2$ and Tu species with changes in the solvent composition. If the change in the ΔG^0 and $T\Delta S^0$ values are due to solvation changes the results given in Table V would indicate that the solute species may be preferentially solvated by formamide by the time the solvent is 40% in that component.

TABLE V

ΔG^0, ΔH^0, AND $T\Delta S^0$ VALUES BASED ON THE MOLE FRACTION SCALE FOR THE REACTION $Hg(CN)_2 + Tu \rightleftharpoons Hg(CN)_2Tu^a$ IN FORMAMIDE–WATER SOLVENT MIXTURES AT 25 °C

Formamide (%, *w/w*)	ΔG^0 (*kcal/mole*)	ΔH^0 (*kcal/mole*)	$T\Delta S^0$ (*kcal/mole*)
0	-0.97 ± 0.08	-1.5 ± 0.1	-0.5 ± 0.1
20	-0.97 ± 0.07	-1.4 ± 0.1	-0.4 ± 0.1
40	-0.66 ± 0.11	-1.7 ± 0.1	-1.0 ± 0.1
60	-0.65 ± 0.11	-1.7 ± 0.1	-1.0 ± 0.1
80	-0.57 ± 0.11	-1.6 ± 0.1	-1.0 ± 0.1
100	-0.50 ± 0.11	-1.5 ± 0.1	-1.0 ± 0.1

[a] The uncertainties are expressed as standard deviations among runs.

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