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Calorimetric Determination of Log K_i, ΔH_i° and ΔS_i° Values for the Interaction of Thiourea with $Hg(CN)_2$ in Water-Formamide Solvents at 25°[1a]

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ABSTRACT

Log K_i, ΔH_i°, and ΔS_i° (i = 1,2) values have been determined calorimetrically at 25°C for the consecutive reaction of thiourea (Tu) with $Hg(CN)_2$ to form $Hg(CN)_2$ Tu_2 in formamide-water solvents. The log K_i, ΔH_i°, and ΔS_i° values determined in 20, 40, 60, 80, and 100 weight percent formamide show little deviation from those in aqueous solution which were determined previously. 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.

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INTRODUCTION

This paper is the second dealing with the effect 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 species are uncharged thereby eliminating the need for activity coefficient and ion pair formation corrections. In the earlier study[2] log K_i, ΔH_i°, and

(2) R. M. Izatt, D. Eatough and J. J. Christensen, J. Phys. Chem., 72, 2720 (1968).

ΔS_i° (i = 1,2) values were reported for reactions (1) and (2) in ethanol-water solvents.

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

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

In that study significant changes were found in the ΔH_i° and ΔS_i° values as the mole fraction of the nonaqueous solvent component was increased indicating the probable formation of solvent-solvent complexes.

In the present investigation reactions (1) and (2) were studied calorimetrically in formamide-water mixtures. Because formamide (D = 109.5[3] at

(3) G. R. Leader, J. Amer. Chem. Soc., 73, 856 (1951).

25°) has solvent properties which are similar[4-6] to those of water and

(4) L. R. Dawson and E. J. Griffith, J. Phys. Chem., 56, 281 (1952).

(5) L. R. Dawson, T. M. Newell and W. J. McCreary, J. Amer. Chem. Soc., 76, 6024 (1954).

(6) J. J. Lagowski, "The Chemistry of Non-Aqueous Solvents ", Academic Press, New York, N.Y., Vol. II, Chapter 5, 1967.

because formamide-water solvents have a high solvation nature, ion pair formation is much less pronounced[7] than in media of lower dielectric

(7) G. Somsen and J. Coops, Rec. Trav. Chim., 84, 985 (1965).

constant such as the ethanol-water mixtures studied previously.

Very few calorimetric or other thermodynamic data have been reported for solvents having dielectric constants greater than that of water. Heats of solution[7], specific heats[8] and densities[8] of aqueous formamide solutions

(8) E. P. Egan and B. B. Luff, J. Chem. Eng. Data, 11, 194 (1966).

have been determined calorimetrically as have heats of solution and solvation for selected electrolytes in HF[9], anhydrous formamide,[7,10] N-methyl-

(9) J. L. Higgens and E. F. Westrum, Jr., J. Phys. Chem., 65, 830 (1961).

(10) K. P. Mishchenko and A. M. Sukhotin, Dokl. Akad. Nauk, USSR., 98, 103 (1954).

formamide[11] and N-methylacetamide.[12] In addition, standard cell potentials,

(11) R. P. Held and C. M. Criss, J. Phys. Chem., 69, 2611 (1965).

(12) L. Weeda and G. Somsen, Rec. Trav. Chim., 86, 263 (1967).

entropies and activity coefficients have been calculated[13-15] from electro-

(13) Reference 6 contains a compilation of electromotive force, conductance, polargraphic and cryoscopic studies carried out in amide solvents.

(14) R. K. Agarwal and B. Nayak, J. Phys. Chem., 71, 2062 (1967).

(15) E. L. Lukeha and C. M. Criss, J. Phys. Chem., 70, 1496 (1966).

motive 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° and ΔS_i° (i = 1,2) values are reported here for reactions (1) and (2) in 20, 60, 80 and 100 weight percent formamide. Comparison is also made with the thermodynamic values valid in ethanol-water solvents which were reported previously.[2]

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.*[16] Each freezing was carried out such that about 80% of

(16) L. R. Dawson, E. D. Wilhoit and P. G. Sears, J. Amer. Chem. Soc., 79, 5906 (1957).

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.

Procedure and Calculations. The thermometric titration technique[17]

(17) J. J. Christensen, R. M. Izatt, L. D. Hansen and J. A. Partridge, J. Phys. Chem., 70, 2003 (1966).

and calorimetric equipment[18] have been described.

(18) J. J. Christensen, R. M. Izatt and L. D. Hansen, Rev. Sci. Instr., 36, 779 (1965).

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° values by means of 7040 and 360 IBM computers using a least squares procedure.[19]

(19) R. M. Izatt, D. Eatough, R. L. Snow, and J. J. Christensen, J. Phys. Chem., 72, 1208 (1968).

Values for the heat capacities and densities at 25° of 20, 40, 60, 80, and 100 weight percent formamide were taken from the literature.[8]

RESULTS

The values of log K_i, ΔH_i° and ΔS_i° (i = 1,2) for reactions (1) and (2) in formamide-water solvents are given in Table I.

DISCUSSION

Examination of the thermodynamic values in Table I reveals the striking fact that the log K_1, log K_2, ΔH_1°, and ΔS_1° 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[4,5,7] that formamide is a water-like solvent.

Dawson and co-workers[4,5] consider the properties of formamide to be of interest because of their striking similarity to those of water. Somsen and Coops[7] 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[20-22] and (b)

(20) K. Schug and A. Dadgar, J. Phys. Chem., 68, 106 (1964).

(21) M. E. Everhard, P. M. Gross, Jr., and J. W. Turner, J. Phys. Chem., 64, 923 (1962).

(22) J. B. Hyne, J. Amer. Chem. Soc., 85, 304 (1963).

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.*,[4,5] However, in a recent X-ray study of KI solutions in formamide, DeSando and Brown[23] present evidence for ion-pair formation

(23) R. J. DeSando and G. H. Brown, J. Phys. Chem., 72, 1088 (1968).

at various concentrations. The possibility of the nonelectrolyte, 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[2] of $Hg(CN)_2$-Tu interaction in ethanol-water solvents the marked change of 2-5 kcal./mole in the ΔH^o and $T\Delta S^o$ values in the 0-50 wt % ethanol region were taken to be indicative of changes in the solvent structure or in solute-solvent interactions or a combination of these. The possibility of similar formamide-H_2O complexes or of changes in solute-solvent interactions appears unlikely in view of the observed leveling effect of the formamide-water solvents.

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Table I

Log K_i, ΔH°_i and ΔS°_i Values for the Stepwise Interaction of Tu with $Hg(CN)_2$ in Formamide-Water Solvent Mixtures Valid at 25° and m = 0.[a]

Weight % Formamide	Log K_1	Log K_2	ΔH_1° kcal/gmole	ΔH_2° kcal/gmole	ΔS_1° cal/gm°C	ΔS_2° cal/gm°C
0	1.97±0.06[b]	0.58±0.04[b]	-1.5±0.1[b]	-7.9±0.2[b]	4.0±0.3[b]	-23.8±0.6[b]
20	2.12±0.03	0.49±0.09	-1.4±0.1	-11.8±0.4	4.9±0.5	-28±1
40	1.91±0.04	0.6±0.1	-1.7±0.1	-10.6±0.4	2.9±0.3	-23±1
60	2.07±0.03	0.59±0.06	-1.6±0.1	-10.6±0.4	4.0±0.4	-23±1
80	2.04±0.05	0.7±0.1	-1.6±0.1	-8.5±0.2	4.1±0.3	-15.8±0.8
100	2.06±0.05	0.6±0.1	-1.33±0.04	-9.7±0.1	5.0±0.2	-20.4±0.4

[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 reference.[8] [b]Ref. 2.