Commun. Fac. Sci. Univ. Ank. Series B
V. 39. pp. 37-44 (1993)

STUDIES ON SOME SUBSTITUTED ARYLFORMAZANS AND THEIR COMPLEXES WITH Ce (III), Th (IV) and U (VI)

O.E. SHERIF, and S.M. ABBASS*

*Chemistry Department, Faculty of Science Cairo University, Giza, Egypt. *Beni Suef.*

(Received May, 12, 1992; Accepted Jan. 6, 1993)

ABSTRACT

Potentiometric and conductimetric studies have been carried out on some substituted 1,5–diaryl–3–acetyl and 3–cyanoformazans and their complexes with Ce (III), The (IV) and UO_2 (VI). The ionization constants of the ligands and formation constants of the complexes are determined potentiometrically. Complexation has also been studied by conductimetric titration method.

INTRODUCTION

Formazans are widely used as analytical reagents (1, 2). They are known as growth stimulant for some plants(3). They are capable for forming chelates which are characterized by their high stability.

Some symmetric cyanoformazans were prepared by reacting the 2–hydroxy–5–sulphophenylhydrazone of cyanoglyoxylic acid with the appropriate diazonium salt. Formation constants of their 1:1 complexes with UO_2^{2+} and C_e^{3+} were determined potentiometrically(4). Complexing of H_g^{2+} with some cyanoformazans was studied potentiometrically(5). Potentiometric, conductimetric, IR, NMR, TGA and magnetic susceptibility have been carried out on La (III) complexes with some symmetric 1,5–diaryl–3–cyanoformazaas. The ionization constants of formazans were also studied(6). The potentiometric study has been carried out in dioxan–water and alcohol–water mixtures and ionic strength 0.1 M ($NaClO_4$). The results indicate the formation of 1:1 and 1:2 complexes.

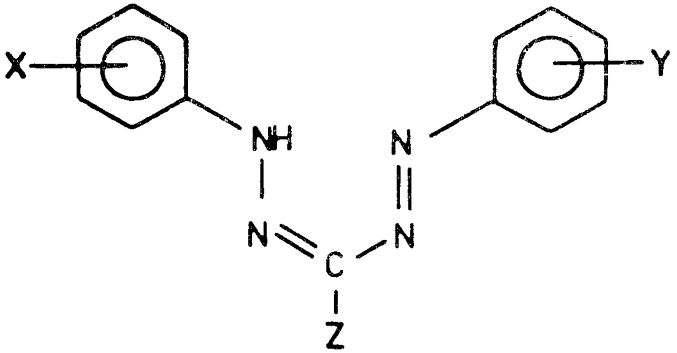
The ionization constants of some acetylformazans and the formation constants of their complexes with lanthanide ions have been determined potentiometrically and conductimetrically (7, 8).

In the psesent study, the stability constants of C_e^{3+}, T_h^{4+} and UO_2^{2+} with some diarylformazans have been determined at 25'C ±

0.1'C and 1.0 M ionic strength using Irving and Rossotti technique(9). Conductimetric titrations were carried out in solutions to get further insight regarding the molecular structure of complexes.

EXPERIMENTAL

All chemicals used in this investigation were of the highest purity available (BDH). The cyano and acetylformazans were repared as previously described(10). The formazans used in this investigation are:



Z = $COCH_2$(I) and $C{\equiv}N$ (II)

X, Y = H, H (a), H, o–COOH (b), H, p–AsO $(OH)_2$(c) and p–AsO $(OH)_2$, p–AsO $(OH)_2$(d).

Stock 10^{-1} M formazan, $CeCl_3 \cdot 6H_2O$, Th $(NO_3)_4$ and $UO_2(CH_3COO)_2 \cdot 2H_2O$ solutions were prepared ant the metal ion solutions were standardized with EDTA using the proper indicator (11–13). The potentiometric titrations were carried as recommended and described elsewhere(9) using a Digital pH–metal Seibold G103 at 25'C.

Conductimetric titrations of 50 ml (4 x 10^{-5} M) formazan solution with standard metal ion solution were carried out using CM–1K conducing meter of 0.975 cell constant.

RESULTS AND DISCUSSION

From the potentiometric results, the $\bar{n}_A$ values (average number of replaceable hydrogens bound to the ligand) were calculated at various pH values. The formation curves relating pH to the corresponding $\bar{n}_A$ values are plotted. The ionization constants of the ionizable functional groups are listed in Table (1). The values were calculated using the

Table 1. The ionization constants of the prepared formazans

Formazan and medium	1 st method					2 nd method					Zean				
	pK_1	pK_2	pK_3	pK_4	pK_5	pK_1	pK_2	pK_3	pK_4	pK_5	pK_1	pK_2	pK_3	pK_4	pK_5
Ib (50 % alc.)(8)	4.37	—	—	—	—	4.5	—	—	—	—	4.44	—	—	—	—
Ib (70 % alc.)	5.02	—	—	—	—	5.1	—	—	—	—	5.06	—	—	—	—
Ic (70 % alc.)	8.32	10.64	—	—	—	8.5	10.6	—	—	—	8.41	10.62	—	—	—
Id (100 % aq.)	4.15	8.3	10.35	11.35	—	4.25	8.55	10.35	11.25	—	4.2	8.42	10.35	11.3	—
IIa (70 % Dioxane)(6)	9.35	—	—	—	—	9.3	—	—	—	—	9.33	—	—	—	—
IIa (70 % alc.)	7.65	—	—	—	—	7.54	—	—	—	—	7.59	—	—	—	—
IIb (70 % alc.)	5.88	10.69	—	—	—	5.85	10.55	—	—	—	5.88	10.62	—	—	—
IIc (70 % DMSO)	6.85	7.95	11.35	—	—	6.9	7.95	11.35	—	—	6.87	7.95	11.35	—	—
IId (40 % DMSO)	5.8	6.9	7.7	9.9	10.6	5.6	6.9	7.75	9.9	10.67	5.7	6.9	7.72	9.9	10.62

A: interpolation at half $\bar{n}_A$ values. B: log term method.

previously described methods(9). The unsubstituted acetylformazan as well as its derivatives reveal that the NH proton is not ionizable. This means that the imino proton is involved in a strong hydrogen bond structure and it is not titrable under our experimental conditions(14). This is in accordance with the previous investigation(7). Meanwhile the unsubstituted cyanoformazan and its derivatives exhibit a pKa corresponding to the ionization of the NH and this can be attributed to the high electron withdrowing effect of the cyano group ($\sigma = + 1.0$)(6). However, the neutralization of the acetyl formazans in the presence of metal ion will release the NH proteon.

The ionization constants of the ionizable groups are greatly affected by solvent and solvent percentage used due to various factors amnng of which are:

1– Dielectric constants of the mixed solvents.

2– The decrease in hydrogen bonding in water by organic solvet.

3– Protonation of the organic solvent.

These factors appeared clearly as follow:

For the mixed solvents, it is found that the pKaCOOH (Ib) in 70 % v / v ethanol–water mixture (5.06) is higher than that in 50 % v / v (4.44)(8) and pKa $AsO(OH)_2$ (IIc) in 70 % v / v DMSO–water mixture (6.87) is higher than that in 40 % v / v (5.70) of (IId). This can be attributed to the decrease in hydrogen bonding as the percentage of the organic solvent increases, consequently the ionization process decreases, hence the pKa value increases. The pKa NH (IIa) in 70 % v / v dioxanewater migxture (9.33)(6) > pK_a NH (IIa) 70 % v / v ethanol–water mixture (7.59) and also the first ionization constant of the arsonic group pKa $AsO(OH)_2$ 70 % v / v ethanol–water mixture Ic (8.41) > pKa $AsO(OH)_2$ of Id in 100 % aqueous medium (4.2). These results are in harmony with the increase of dielectric constant of the medium as mentioned by Gergely(15) who indicated that dioxane molecules break the hydrogen bonded structure of water. It is expected that the extent of hydrogen bonding in ethanol–water mixtures > dioxane–water mixture and also hydrogen bonding in water > DMSO water mixtures and these results follow the acidity order(16). The effect of protonation of solvent appeared clearly on titrating formazan (IIc) in DMF–water mixture where the results obtained were unacceptable. This may be explained on the basis that HCl protonates the DMF molecules affecting the shape of the titration curves and interfering in the titration of the ligand and even the free HCl.

Comparing the effect of cyano and acetyl groups on the ionizable groups, it is found that the pKa NH (Ia) is so high that its exact value could not be obtained under our experimental conditions where it was expected to be above 14(14) while the NH proton is titrable in case of cyanoformazans (IIa) as previously discussed.

From the titration curves of the mixtures containing the ligand and the metal ions, the average number of ligands (n) attached to the metal ion and the free ligand exponent (pL) were calculated and plotted against each other to produce the formation curves of the metal complexes. The $\bar{n}$ values extend to 2.0 for all complexes indicating that 1:1 and 1:2 (M:L) complexes are formed in solution. The stability constants log K_2, log K_1 and log β_2 were calculated (Table 2) using the equations given by Irving and Rossotti(9). The methods used for cal-

Table 2. Commulative data of log β_1 and log β_2 values for the chelates under investigation.

Formazan and medium	log β_1				log β_2				
	A	B	C	mean	A	B	C	D	mean
Complexes with Ce^{3+}									
Ib (70 % alc.)	5.5	5.09	5.26	5.28	10.38	10.35	10.37	10.34	10.36
Ic (70 % alc.)	8.8	8.66	8.63	8.69	16.8	17.01	16.8	17.4	17.0
Id (100 % aq.)	5.88	5.8	5.54	5.74	11.35	12.18	11.34	11.24	11.52
IIa (70 % alc.)	7.85	7.61	7.58	7.68	15.15	15.13	15.15	15.1	15.13
IIb (70 % alc.)	6.66	6.41	6.59	6.55	12.06	11.88	12.06	11.4	11.85
IIc (70 % DMSO)	5.95	5.75	5.88	5.86	10.68	10.67	10.69	10.5	10.63
IId (40 % DMSO)	5.74	5.57	5.44	5.58	10.99	10.97	10.98	11.9	10.96
Complexes with Th^{4+}									
Ib (70 % alc.)	6.27	6.17	5.91	6.11	12.17	12.23	12.18	12.24	12.20
Ic (70 % alc.)	8.96	8.85	8.6	8.8	17.75	17.59	17.57	17.6	17.62
Id (100 % aq.)	6.42	6.06	6.00	6.16	12.57	12.64	12.57	12.58	12.59
IIa (70 % alc.)	7.64	7.28	7.17	7.36	15.09	15.09	15.09	15.18	15.11
IIb (70 % alc.)	6.67	6.45	6.33	6.48	12.92	12.92	12.9	12.92	12.91
IIc (70 % DMSO)	6.03	5.89	5.69	5.87	11.77	11.65	11.66	11.70	11.66
IId (40 % DMSO)	6.15	6.04	6.01	6.06	11.40	11.27	11.40	11.06	11.28
Complexes with UO_2^{2+}									
Ib (70 % alc.)	5.11	4.80	4.66	4.85	9.99	10.01	9.98	10.06	10.01
Ic (70 % alc.)	8.48	8.13	8.27	8.29	16.28	16.11	16.28	15.84	16.12
Id (100 % aq.)	5.41	5.31	5.64	5.45	10.62	10.67	10.65	10.56	10.64
IIa (70 % alc.)	7.38	7.21	7.12	7.23	14.2	14.24	12.2	14.08	14.18
IIb (70 % alc.)	6.06	6.17	5.7	5.97	11.74	12.02	11.37	11.52	11.66
IIc (70 % DMSO)	5.24	5.21	5.08	5.17	9.64	9.72	9.64	10.00	9.74
IId (40 % DMSO)	5.54	5.49	5.35	5.46	10.34	10.29	10.34	10.26	10.3

A: interpolation at half $\bar{n}$ values B: Correction term method

C: successive approximation method D: mid point method.

culating successive stability constants were, interpolation at the half $\bar{n}$ value (A), correction term (B), successive approximations (C) and mid–point methods (D)(9).

The results show that the order of stabilities of the metal–formazan complexes follows the order:

$Th^{4+} > C_e^{3+} > UO_2^{2+}$ and this can be attributed to some factors which may be summarized as follows:

1– In complex formation, the affinity for chelation hence, the stability constants increase mostly by increase of the ionic charge of the central metal ion(17).

2– Generally, the stability constants of metal chelates increase with decreasing of ionic size. This is in harmony with simple electrostatic theory. This is in accordance with the results obtained for Th complexes which have the highest stability constants. This can be explained as Th^{4+} has the smallest ioic size [ionic radius: C_e^{3+} (1.034), Th^{4+} (1.02) and U^{6+} (0.8)] taking into consideration the presence of two oxygen atoms attached to the uranium ion resulting in increase the size of the central uranyl ion.

3– The electronegativity (E.N.) of the central metal ion; where, as the electronegativity increases the ionization potential increases hence, the metal affinity for chelation increases and this is in full agreement for C_e^{3+} and Th^{4+} [E.N. 1.12 and 1.30, respectively] (18). It is not quite right to include U(VI) in this comparison since the investigated ion is in this form of UO_2^{2+}.

Comparison of the results reveals that formazan (Ic) has higher affinitiy for chelation than the other formazans. Since it is weaker acid than the others, its conjugate base L^{2-} will be stronger with a higher chelating affinity and higher stability in its complexes. It could be noted that the formazan (IIa) complexes have relatively high stability compared to other complexes. This is due to the covalent bond character in these complexes, in addition no steric effect is present. The low stability of formazans (Id) and (IId) complexes can be explained on the basis that the formazans (Id) and (IId) have many coordination sites but they can not participate altogether in chelation. The release of the undissociated proton of the $AsO(OH)_2$ group requires a relatively high pH which was not attained actually to avoid hydrolysis of the formed complexes. In other words, the hydroxyl group of the arsonic groups of lower pK value is the one involved in chelation. The low stability constants of(Id) complexes may also be attrbutited to the strong electron withdrawal effect exerted by the two p–arsonic groups and to the fact that the titrations were carried out in aqueous medium which may assist the complex hydrolysis.

The formazans IIb, IIc and IId complexes follow the order IIb > IIc > IId. The higher stability of the complexes can be attributed to solvent effects where its complexes are formed in alcoholic medium whose tendency for hydrogen bond formation is higher than that in DMSO medium. This assists the ionization of the ionizable functional groups, hence, increasing the stability of metal–formazan (IIb) complexes. It could also be seen that the stability constants of metalformazan chelates for IIb is higher than that of (Ib). This can be explained as the electronegativity of the cyanogroups in cyanoformazan stabilizes the carboxylate anion hence, increasing the tendency for metal–formazan bond formation resulting in increasing the stability of cyanoformazan complexes more than of acetylformazan. [The medium is 70 % alcohol–water in both cases].

Conductimetric titrations

The conductimetric titration curves indicate the increase of conductance with adding the metal ion solution is mainly due to the release of the highly conducting H^+ ions with the metal ion thus:

$$2\,HL + M^{n+} \rightleftarrows \underset{1:2}{[ML_2]}^{(n-2)} + 2H^+$$

Further addition of metal ions, after complete conversion of HL to 1:2 species, will produce a new 1:1 species thus:

$$\underset{1:2}{ML_2} + M \rightleftarrows \underset{1:1}{2\,ML}$$

The conductimetric titration curves for the complexes show two breaks at molar ratio of 1:1 and 1:2 indicating the formation of two types of complexes with stoichiometric ratios 1:1 and 1:2 (M:L) which is in accordance with the results obtained from pH-metric titrations.

The higher molar ratios can be excluded due to steric hinderance in accomodating more than two formazan molecules around a metal ion and steric geometry of formazan itself. This also can be attributed to the effect of solvent–water medium in which the metal ion exists almost as aquo complex where further coordination by a third molecule of formazan is inhibited by the strongly bound water molecules.

REFERENCES

1. VASILEVA, N.L. and ERMAKOVA, M.I., Zh Analit. Khim., 18, 43 (1963).
2. YU, JU CH'in, Ki, PE-CH'i and CHANG CHIOWU., K'O Hsuch T'ung Pao, 10, 616, (1965) [C.A. 66: 8070u (1967)].
3. BALUT, D., ZAWISTOWSKA, M. and ECKSTEIN, Z., Bull. Acad. Polon Sci., Ser. Chim., 14, 11 (1966).
4. SHIKHOVA, I.A., Tr. INST. KHIM., Ural. Nauchn, Akad. Nauk SSSR, 30, 18 (1974). [C.A.: 84, 112419j (1976)].
5. ERMAKOVA, M.I. and LATOSH, N.I., Tr. Inst. Khim., Ural Nauchn. Tsentre Akad. Nauk. SSSR, 30, 47 (1974). [C.A.: 84: 96193y (1976)].
6. ABDEL-GHANI, N.T., and SHERIF, O.E., Thermochem. Acta, 156, 69 (1989).
7. BADAWY, S.S., ISSA, Y.M. and ABDEL, FATTAH., H.M., Trans. Met. Chem., 14, 401 (1989).
8. ANSARY, A.L., RIZAK, M.S., ISSA, Y.M., and ABDEL FATTAH, H.M., Egypt J. Chem. (in press).
9. IRVING, H. and ROSSOTTI, H.S., J. Chem. Soc., 3397 (1953), 2904 (1954).
10. YAO, H.C., J. Org. Chem., 29, 2959 (1964).
11. VOGEL, A.I., "Text book of Quantitative Inorganic analysis" 3rd Edit., Longmans, London, 442 (1972).
12. FRITZ, J.S., OLIVER, R.T. and PIETRZYK, D.J., Anal. Chem., 30, 1111 (1958).
13. KINNUNEN, J. and WENNERSTRAND, B., Chemist. Analyst., 46, 92 (1957).
14. GILL, J.B., IRVING, H.N.H. and PRESCOTT, J. Chem. Soc. Perkin Trans., 13, 1983 (1977).
15. GERGELY, A. and KISS, T.J., J. Inorg. Nucl. Chem., 39, 109, (1977).
16. KRESHKOV, A.P., Talanta, 17, 1029 (1970).
17. ABDEL-KADER, A.K., ABU-EL-WAFA, S.M. and EZZEL-ARAB, M.A., J. Chin. Chem. Soc., 30, 225 (1983).
18. WEST, R.C., "Handbook of Chemistry and Physics", The Chemical Rubber Company 59 *th* Edit. Chio, USA (1978-1979).