

Studies on the Stability of Vanadyl Chelates with Dithiodiacetic Acid and Diglycollic Acid*

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The proton-ligand stability constants of DTDA and DGA and the stepwise stability constants of their chelates with VO(IV) have been determined in aqueous medium by potentiometric method at different ionic strengths, (0.1, 0.2 and 0.3M NaClO₄) and temperatures (25° and 35°). Thermodynamic stability constants and thermodynamic parameters (ΔG° , ΔH° and ΔS°) have been calculated.

THE survey of the literature reveals that the formation constants of DTDA and DGA with few metals¹⁻² have been reported. However no attempt appears to have been made on the vanadyl chelates with these ligands. The present paper reports the formation of 1 : 1 and 1 : 2 complexes of VO(IV) with the above mentioned ligands.

Experimental

The solutions of DTDA (Evans' Chematics), DGA (John Baker Inc., Colorado, U. S. A.) and vanadyl sulphate (VOSO₄ · 2H₂O Reachim USSR) were freshly prepared in double distilled water. Perchloric acid (0.04M) was prepared by diluting a calculated quantity of the acid with distilled water. Other chemicals used were of A.R. Grade.

Apparatus :

The pH measurements were recorded with a Philips pH meter (PR9405 M) with glass and calomel electrodes at 25° ± 0.5° and 35° ± 0.5° (maintained in a thermostat). The instrument was calibrated using 0.05M potassium hydrogen phthalate.

Titration procedure :

The titrations were carried out in a specially designed double walled beaker of the capacity of 250 ml made of pyrex glass using Calvin-Bjerrum^{3,4} titration technique as modified by Irving and Rossotti⁶. All the experiments were carried out in an inert atmosphere of nitrogen by bubbling the gas through the solution, during the course of titrations. Titrations were performed in duplicate in order to establish the reproducibility of the measurements.

Results and Discussion

Proton-ligand stability constants of DTDA and DGA and the stepwise formation constants of their chelates with vanadyl (IV) were determined using

Calvin-Bjerrum technique as modified by Irving and Rossotti. pH range investigated for VO (IV)-DTDA and VO(IV)-DGA systems were 2.25-3.25 and 2.25-3.00 respectively. In the pH range mentioned above, factors like hydrolysis of vanadyl ion and the presence of polynuclear species were assumed to be absent, and it is because of :

- (i) the departure of the metal chelate titration curve from the ligand titration curve commencing at about pH 2.25 which is below the pH of hydrolysis of the metal ion, and
- (ii) the solutions employed under the experimental conditions were very dilute.

Values obtained at half \bar{n}_A and \bar{n} were further computed using the following techniques^{5,7}

- (i) Curve-fitting method
- (ii) Correction term method
- (iii) Pointwise calculation method

The final values of proton-ligand stability constants, $\log K_1^H$ and $\log K_2^H$, and metal ligand formation constants, $\log K_1$ and $\log K_2$ are given in Table 1. The thermodynamic stability constants were determined by extrapolating the values to zero ionic strength and the values are given at the bottom of the Table 1.

The thermodynamic parameters ΔG° , ΔH° and ΔS° of complexation reactions were calculated at 25° and 35° by using standard equations⁸. The values are tabulated in Table 2.

The values of \bar{n} in the metal-ligand formation curve varies between 0.2 and 1.9, thereby indicating the formation of 1 : 1 and 1 : 2 complexes. A comparison of the stepwise formation constants indicates that the values are slightly higher at 25°

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TABLE 1—PROTON LIGAND STABILITY CONSTANTS OF DTDA A AND DGA AND FORMATION CONSTANTS OF THEIR CHELATES WITH VO(IV)

Ligands used	Ionic concentration (μ)											
	0.1M(25°C)			0.2M(25°C)			0.3M(25°C)			0.1M(35°C)		
	$\log K_1^H$	$\log K_2^H$	$\log \beta_2^H$	$\log K_1^H$	$\log K_2^H$	$\log \beta_2^H$	$\log K_1^H$	$\log K_2^H$	$\log \beta_2^H$	$\log K_1^H$	$\log K_2^H$	$\log \beta_2^H$
DTDAA	3.96	2.82	6.78	3.82	2.66	6.48	3.66	2.62	6.28	3.98	2.83	6.81
DGA	4.05	2.63	6.68	3.94	2.49	6.43	3.84	2.42	6.26	4.06	2.64	6.70
	$\log K_1$	$\log K_2$	$\log \beta_2$	$\log K_1$	$\log K_2$	$\log \beta_2$	$\log K_1$	$\log K_2$	$\log \beta_2$	$\log K_1$	$\log K_2$	$\log \beta_2$
DTDAA	2.55	1.53	4.08	2.70	1.70	4.40	2.85	1.85	4.70	2.47	1.51	3.98
DGA	3.10	2.06	5.16	3.18	2.16	5.34	3.30	2.28	5.58	3.02	2.06	5.08

The thermodynamic stability constants $\log K_1^{\mu=0}$ and $\log K_2^{\mu=0}$ (DTDAA) ; $\log K_1^{\mu=0}$ and $\log K_2^{\mu=0}$ (DGA) were found to be 2.39, 1.37 and 3.01, 1.95 respectively.

TABLE 2—THERMODYNAMIC PARAMETERS OF THE COMPLEXES ($\mu=0.1M$)

Ligand used	Temp. °C	ΔG° (kcal.mole ⁻¹)			ΔH° (kcal.mole ⁻¹)			ΔS° (cal.mole ⁻¹ .deg ⁻¹)		
		ΔG_1°	ΔG_2°	ΔG°	ΔH_1°	ΔH_2°	ΔH°	ΔS_1°	ΔS_2°	ΔS°
DTDAA	25°	-3.44	-2.07	-5.51	-3.36	-0.84	-4.20	0.26	4.06	4.32
	35°	-3.48	-2.13	-5.61						
DGA	25°	-4.20	-2.78	-6.98	-3.78	-0.00	-3.78	1.38	9.17	10.55
	35°	-4.26	-2.90	-7.16						

as compared to 35° i.e., lower temperature is favourable for complex formation. At a particular ionic strength and temperature the stability order is the same as the order of the basicity of the ligands, i.e., DGA > DTDAA.

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