Thermochimica Acta, 45 (1981) 121—123
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

Note

STABILITY CONSTANTS AND THERMODYNAMIC FUNCTIONS OF BERYLLIUM(II), PALLADIUM(II) AND OXOZIRCONIUM(II) WITH LAPACHOL [2-HYDROXY-3-(3-METHYL-2-BUTENYL)-1,4-NAPHTHOQUINONE]

B.M.L. BHATIA * and S.S. SAWHNEY

Chemistry Department, D.A.V. (P.G.) College, Dehra Dun, 248001 (India)

(Received 29 September 1980)

Chelating properties of lapachol are known [1—3]. This communication concerns the determination of stability constants and thermodynamic functions of beryllium(II)-, palladium(II)- and oxozirconium(II)—lapachol systems.

EXPERIMENTAL

All chemicals used were either BDH or Aldrich Analar quality. The ligand solutions in ethanol and metal nitrate/chloride in CO_2-free conductivity water were prepared. pH Metric titrations were carried out with carbonate-free 0.2 M NaOH. The concentration of the ligand and metal ion was always 5×10^{-2} M and 0.5×10^{-2} M, respectively. An appropriate quantity of KCl/KNO_3 (1.0 M) was added to maintain a constant ionic strength of 0.1 M. The stability constants of the metal- and proton-complexes were estimated at $20 \pm 0.5°C$ and $40 \pm 0.5°C$ in a thermostat bath using the Irving—Rossotti method [4], a modification of Bjerrum's technique. pH Measurement was made on a Metrohm-Harsau pH meter which had a sensitivity of ±0.05 and was calibrated with a suitable buffer before use. At the end of each titration the curve of volume of sodium hydroxide consumed and corresponding pH was drawn. The shape of the curve was as usual. Correction due to Van Uitert and Haas [5] for 50% v/v ethanol—water mixture was applied.

RESULTS AND DISCUSSION

$\bar{n}_H$, $\bar{n}$, and pL were calculated for different systems using the expressions of Irving and Rossotti [4]. The metal—ligand stability constants were estimated by the least-squares method and the following equations were used for their

* Address for correspondence: Additive Laboratory, Indian Institute of Petroleum, Dehra Dun, 248005, India.

0040-6031/81/0000—0000/$02.50

TABLE 1

Protonation constant of the ligand and overall metal–ligand stability constants of the chelates and thermodynamic functions at two temperatures

Metal ion	Protonation constant metal–ligand stability constants	Temperature (°C)		ΔG^0 (kcal mole^{-1})		ΔH^0 (kcal mole^{-1})	ΔS^0 (cal mole^{-1} °C^{-1})
		20	40	20°C	40°C		
	$\log {}^{p}K^{H2}$	6.450	5.850				
Be(II)	$\log k_1$	3.895	3.675	−5.32	−5.27		
	$\log k_2$	3.620	3.270	−4.85	−4.68		
	$\log \beta_2$	7.515	6.945	−10.17	−9.95	−11.96	−6.42
Pd(II)	$\log k_1$	4.645	5.150	−6.22	−7.35		
	$\log k_2$	3.295	3.790	−4.41	−5.44		
	$\log \beta_2$	7.940	8.940	−10.63	−12.79	+20.98	+107.88
ZrO(II)	$\log k_1$	4.740	4.820	−6.36	−6.90		
	$\log k_2$	3.370	3.450	−4.51	−4.95		
	$\log \beta_2$	8.110	8.270	−10.87	−11.85	+3.3	48.40

determination by the point-wise method [6]

$$\log k_1 = \mathrm{pL} - \log \frac{1-\bar{n}}{\bar{n}}$$

$$\log k_2 = \mathrm{pL} - \log \frac{2-\bar{n}}{\bar{n}-1}$$

The overall changes in free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) have been determined using the well-known temperature coefficient and the Gibbs—Helmholtz equation [7]. The mean values of protonation constant, stability constants and thermodynamic functions are given in Table 1.

The value of $\bar{n}$ approaches 2 for Be(II), Pd(II) and ZrO(II) chelates with lapachol, indicating the formation of 1 : 1 and 1 : 2 complexes. The data for the Be(II)—lapachol chelate reveal a decrease in value of $\log {}^{\mathrm{p}}K^{\mathrm{H}}$, $\log k_1$ and $\log k_2$ with increase of temperature. This indicates that a lower temperature is favourable for complexation because of the decrease in number of collisions with the decrease in kinetic energy of molecules, and thus stability is lowered. In the case of Pd(II) and ZrO(II)—lapachol systems, an increase in the values of $\log k_1$ and $\log k_2$ was observed, indicating that a high temperature favours the reaction. The formation of complexes, with the exception of Pd(II)— and ZrO(II)—lapachol reactions which are endothermic in nature, providing an explanation for increase in the value of formation constants with increase of temperature, is exothermic, thereby supporting the lower values of formation constants with growth of temperature. The free energies of formation have more negative values, with the exception of the Be(II)—lapachol system, as temperature increases, showing that complex formation is a spontaneous process. The entropy (ΔS^0) values are positive in Pd(II)— and ZrO(II)—lapachol systems, indicating a favourable entropy for the formation of complexes. The negative entropy value for the Be(II)—lapachol system is not favourable.

REFERENCES

1 C.G. DeLima, F.T. Araujo, A. DuFresne and J. Knudsen, Inorg. Nucl. Chem. Lett., 7(6) (1971) 513.
2 S.S. Sawhney and B.M.L. Bhatia, Thermochim. Acta, 42 (1981) 105.
3 S.S. Sawhney and S.D. Matta, J. Indian Chem. Soc., 57 (1980) 497.
4 H. Irving and H. Rossotti, J. Chem. Soc., (1954) 2904.
5 L.G. Van Uitert and C.G. Haas, J. Am. Chem. Soc., 75 (1953) 451.
6 H. Irving and H. Rossotti, J. Chem. Soc., (1953) 3397.
7 S. Glasstone, Thermodynamics for Chemists, Van Nostrand, Princeton, 1960.