

Potentiometric and Thermodynamic Studies of Vinylacetic Acid and Its Metal Complexes in Monomeric and Polymeric Forms

Ahmed A. Al-Sarawy

Department of Mathematics and Physical Science, Faculty of Engineering, Mansoura University, Mansoura, Egypt

Received 29 August 2003; accepted 29 March 2004

DOI 10.1002/app.21337

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Proton–monomeric ligand dissociation and metal–monomeric ligand stability constants of vinylacetic acid (VA) with some metal ions were calculated potentiometrically in 0.1M KCl. Also, in the presence of 2,2'-azobisisobutyronitrile as initiator, the proton–polymeric ligand dissociation and metal–polymeric ligand stability constants were calculated. The effect of temperature on the dissociation of VA and the stability of its formed complexes were studied in monomeric and polymeric forms. The corre-

sponding thermodynamic functions were derived and discussed. The dissociation process was nonspontaneous, endothermic, and entropically unfavorable. The formation of the metal complexes was found to be spontaneous, endothermic, and entropically favorable. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 952–956, 2005

Key words: thermodynamics; dissociation; stabilization; metal–polymer complexes; hydrophilicity

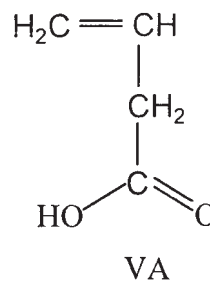
INTRODUCTION

In solution, polymeric ligands are used to bind with selectivity a specific metal ion from a mixture and to isolate important metals from seawater and wastewater.^{1,2} Several significant criteria for facile metal ion removal from aqueous solution include the hydrophilicity of the organic ligand when it is anchored to a hydrophobic, pH-stable polymer backbone such as modified, kinetics, and thermodynamics of the pendant ligand reaction with the selected metal ion.^{3,4} Marinski and Reddy⁴ and Van den Hoop et al.⁵ studied the potentiometric titration of polyacrylic acid and polymethacrylic acid in the presence of an excess amount of 1 : 1 salt and trace concentrations of Co^{2+} , Zn^{2+} , and Cd^{2+} ions.

In the present article, we describe the dissociation constant of vinylacetic acid and the stability constants for its complexes with Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , and Hg^{2+} in monomeric and polymeric forms, which were obtained by potentiometric studies. Furthermore, the corresponding thermodynamic functions of dissociation and complexation are derived and discussed.

EXPERIMENTAL

Vinylacetic acid (VA) was used without purification as received (Aldrich, Milwaukee, WI).



The monomeric ligand solution (0.01M) was prepared by dissolving an accurate mass of the solid in doubly distilled water. Metal ion solutions (0.002M) were prepared from AnalaR metal chlorides (BDH, Toronto, Canada) in doubly distilled water and standardized with EDTA.⁷ A solution of 2,2'-azobisisobutyronitrile (AIBN) as initiator (0.005M) was prepared by dissolving an accurate mass of the solid in ethanol (AnalaR). Solutions of 0.01M HCl and 1M KCl were prepared in doubly distilled water. A carbonate-free sodium hydroxide solution in doubly distilled water was used as titrant and standardized against AnalaR oxalic acid.

The apparatus, general conditions, and methods of calculation were the same as those described in previous works.^{3,8,9} The following mixtures were prepared and titrated potentiometrically against standard

Correspondence to: alsarawy2000@yahoo.com.

TABLE I
Thermodynamic Functions for the Dissociation of VA and PVA in Doubly Distilled Water and 0.1M KCl^a

Compound	Temperature (K)	Dissociation constant, pK_1^H	Gibbs energy change, ΔG_1 (kJ mol ⁻¹)	Enthalpy change, ΔH_1 (kJ mol ⁻¹)	Entropy change, $-\Delta S_1$ (J mol ⁻¹ K ⁻¹)
VA	298	4.35	24.82	20.87	13.26
	308	4.23	24.95		13.25
	318	4.12	25.09		13.27
PVA	328	4.86	30.52	26.59	11.98
	338	4.74	30.68		12.10
	348	4.61	30.72		11.87

^a The values given present an average of three measurements.

0.01M NaOH in doubly distilled water mixture at 298, 308, and 318 K, respectively.

1. 5 mL 0.01M HCl + 5 mL 1M KCl
2. 5 mL 0.01M HCl + 5 mL 1M KCl + 5 mL 0.01M VA
3. 5 mL 0.01M HCl + 5 mL 1M KCl + 5 mL 0.01M VA + 5 mL 0.002M metal chloride

For each mixture, the volume was made up to 50 mL with doubly distilled water before the titration. These titrations were repeated in the presence of 1 mL 0.005M AIBN as initiator for the polymerization of vinylacetic acid¹⁰ and at 328, 338, and 348 K, respectively. A constant temperature was maintained to 0.05 K by using an ultrathermostat (Sanyo Gallenkamp thermostirrer 85, Loughborough, UK). The pH measurements were carried out using VWR Scientific Instruments (Boston, MA) model 8000 pH meter accurate to ± 0.01 units.

RESULTS AND DISCUSSION

The average number of the protons associated with the reagent molecule \bar{n}_A in monomeric (VA) and polymeric (PVA) forms was determined at different pH values applying the following equation:

$$\bar{n}_A = Y + \frac{(V_1 - V_2)(N^0 + E^0)}{(V^0 - V_1)TC_L^0} \quad (1)$$

where V_1 and V_2 are the volume of alkali required to reach the same pH in the titration curves of hydrochloric acid and reagent, respectively; V^0 is the initial volume (50 cm³) of the mixtures; TC_L^0 is the total concentration of the reagent; N^0 is the molarity of sodium hydroxide solution; and E^0 is the initial concentration of the free acid. Thus, the formation curves (\bar{n}_A versus pH) for the proton-ligand systems were constructed and found to extend between 0 and 1 in the \bar{n}_A scale. This means that VA and PVA have one dissociable proton, the enolized hydrogen ion of the carboxylic group (COOH, pK_1^H). Different computational methods¹¹ were applied to evaluate the disso-

ciation constants. The experiments were replicated three times, and the average values obtained are listed in Table I.

The PVA has a lower acidic character (higher pK_1^H values) than that of VA. This is quite reasonable because the presence of the vinyl group (H₂C=CH—) in the monomeric form will decrease the electron density, whereby weaker O—H bonds are formed.^{1,3,6} The absence of the vinyl group in the polymeric form will lead to the opposite effect (i.e., retarding the removal of the ligand proton and thus increasing the basicity of PVA).

The formation curves for the metal complexes were obtained by plotting the average number of ligands in both monomeric and polymeric forms, respectively, attached per metal ion (\bar{n}) versus the free ligand exponent (pL), according to Irving and Rossotti.¹² These curves were analyzed and calculated using the following equations:

$$\bar{n} = \frac{(V_3 - V_2)(N^0 + E^0)}{(V^0 - V_2)\bar{n}_A TC_M^0} \quad (2)$$

and

$$pL = \log_{10} \frac{\sum_{n=0}^{\infty} \beta_n^H \left(\frac{1}{\text{antilog pH}} \right)^n}{TC_L^0 - \bar{n} TC_M^0} \frac{V^0 + V_3}{V^0} \quad (3)$$

where TC_M^0 is the total concentration of the metal ions present in the solution, and β_n^H is the overall proton-reagent stability constant. V_1 , V_2 , and V_3 are the volumes of alkali required to reach the same pH in the titration curves of hydrochloric acid, organic ligand, and complex, respectively. These curves were analyzed and the successive stability constants were determined using different computational methods.^{13,14} The values of the stability constants ($\log K_1$ and $\log K_2$) are given in Tables II and III. The following general remarks can be made:

1. The maximum \bar{n} values in all cases were found to be $\cong 2$, revealing that both ML and ML₂ types of complexes are formed in solution.¹⁵

TABLE II
Stepwise Stability Constants for the Complexes ML and ML₂ of VA in Doubly Distilled Water and 0.1M KCl at Different Temperatures^a

M ⁿ⁺	298 K		308 K		318 K	
	log K ₁	log K ₂	log K ₁	log K ₂	log K ₁	log K ₂
Mn ²⁺	3.94	3.40	4.16	3.55	4.37	3.70
Co ²⁺	4.15	3.70	4.41	3.92	4.67	4.17
Ni ²⁺	4.24	3.78	4.47	3.99	4.70	4.23
Cu ²⁺	4.35	3.92	4.56	4.14	4.77	4.36
Zn ²⁺	4.49	4.03	4.66	4.21	4.83	4.40
Cd ²⁺	4.60	4.14	4.79	4.30	4.88	4.46
Hg ²⁺	4.74	4.20	4.93	4.73	5.03	4.54

^a The values given present an average of three measurements.

- No precipitate was observed in the titration vessel, indicating that the possibility of formation of metal hydroxide can be excluded.¹⁶
- For all complexes, the stability constants of PVA are higher than those of VA. This is quite reasonable because the ligand in polymeric form is a better complexing agent.^{1,3,4}
- The decrease of the values of stability constants of the metal complexes of VA and PVA was found to be in the order Hg²⁺ > Cd²⁺ > Zn²⁺ > Cu²⁺ > Ni²⁺ > Co²⁺ > Mn²⁺.¹⁷

The dissociation constants (pK^H) for VA and PVA as well as the stability constants of their complexes with Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, and Hg²⁺ were evaluated at different temperatures and are given in Tables I, IV, and V. The slope of the plot (pK₁^H or log K versus 1/T) was used to evaluate the enthalpy change (ΔH) for the dissociation or complexation process, respectively. From the Gibbs energy change ΔG and ΔH values one can deduce the entropy change ΔS using the following well-known relationships:

$$\Delta G = -2.303RT \log K = 2.303RT \text{ p}K \quad (4)$$

$$\Delta S = (\Delta H - \Delta G)/T \quad (5)$$

All thermodynamic parameters of the dissociation process of VA and PVA are recorded in Table I. Inspection of these values reveals the following:

- The pK^H values decrease with increasing temperature, revealing that their acidity increases with increasing temperature.
- A positive value of ΔH indicates that its dissociation is accompanied by adsorption of heat and the process is endothermic.
- A large positive value of ΔG indicates that the dissociation process is not spontaneous.
- A negative value of ΔS is obtained because of the increased order resulting from solvation processes.

All the thermodynamic parameters of the stepwise stability constants of VA and PVA complexes are recorded in Tables IV and V. It is known that the divalent metal ions exist in solution as octahedrally hydrated species¹⁴ and the obtained values of ΔH and ΔS can then be considered as a sum of two contributions: (1) release of H₂O molecules, and (2) metal-ligand bond formation.

It was suggested¹⁸ that the ions in aqueous solution order the water molecules around them and during complex formation between oppositely charged ions (ligand L⁻ and Mⁿ⁺) will lead to the breakdown of

TABLE III
Stepwise Stability Constants for the Complexes ML and ML₂ of PVA in Doubly Distilled Water and 0.1M KCl at Different Temperatures^a

M ⁿ⁺	328 K		338 K		348 K	
	log K ₁	log K ₂	log K ₁	log K ₂	log K ₁	log K ₂
Mn ²⁺	5.40	4.82	5.62	5.05	5.82	5.25
Co ²⁺	5.65	5.23	2.85	5.40	6.04	5.58
Ni ²⁺	5.79	5.31	5.98	5.52	6.18	5.72
Cu ²⁺	5.95	5.51	6.15	5.70	6.34	5.90
Zn ²⁺	6.05	5.55	6.26	5.77	6.45	5.98
Cd ²⁺	6.21	5.67	6.39	5.85	6.56	6.04
Hg ²⁺	6.28	5.76	6.45	5.94	6.63	6.13

^a The values given present an average of three measurements.

TABLE IV
Thermodynamic Functions for the Complexes ML and ML₂ of VA in
Doubly Distilled Water and 0.1M KCl

M ⁿ⁺	T (K)	Gibbs energy change (kJ mol ⁻¹)		Enthalpy change (kJ mol ⁻¹)		Entropy change (J mol ⁻¹ K ⁻¹)	
		-ΔG ₁	-ΔG ₂	ΔH ₁	ΔH ₂	ΔS ₁	ΔS ₂
Mn ²⁺	298	22.48	19.40			206.37	156.44
	308	24.53	20.94	39.02	27.22	206.33	156.36
	318	26.61	22.53			206.38	156.45
Co ²⁺	298	23.67	21.11			237.78	213.95
	308	26.00	23.11	47.19	42.65	237.62	213.50
	318	28.43	25.39			237.79	213.96
Ni ²⁺	298	24.19	21.56			221.24	209.36
	308	26.36	23.53	41.74	40.83	221.10	208.96
	318	28.61	25.75			221.22	209.37
Cu ²⁺	298	24.82	22.36			211.17	209.02
	308	26.89	24.41	38.11	39.93	211.03	208.89
	318	29.04	26.54			211.16	209.02
Zn ²⁺	298	25.61	22.99			189.46	190.73
	308	27.48	24.82	30.85	33.58	189.38	190.48
	318	29.40	26.79			189.46	190.69
Cd ²⁺	298	26.24	23.62			173.32	176.71
	308	28.24	25.35	25.41	29.04	174.18	176.59
	318	29.71	27.15			173.33	176.69
Hg ²⁺	298	27.04	23.96			179.06	183.92
	308	29.07	25.74	26.32	30.85	179.83	183.83
	318	30.62	27.64			179.05	183.93

metal-water arrangement, resulting in positive entropy and enthalpy changes. Examination of these values shows the following:

1. The stepwise stability constants (log K₁ and log K₂) for VA and PVA complexes increase with increasing temperature in the case of Mn²⁺,

TABLE V
Thermodynamic Functions for the Complexes ML and ML₂ of PVA in
Doubly Distilled Water and 0.1M KCl

M ⁿ⁺	T (K)	Gibbs energy change (kJ mol ⁻¹)		Enthalpy change (kJ mol ⁻¹)		Entropy change (J mol ⁻¹ K ⁻¹)	
		-ΔG ₁	-ΔG ₂	ΔH ₁	ΔH ₂	ΔS ₁	ΔS ₂
Mn ²⁺	298	33.91	30.27			239.60	231.74
	308	36.37	32.68	49.68	45.74	239.79	232.01
	318	33.78	34.98			239.83	231.95
Co ²⁺	298	33.91	32.84			229.84	213.62
	308	18.44	34.94	41.48	37.23	177.27	213.52
	318	40.24	37.18			234.82	213.82
Ni ²⁺	298	36.36	33.34			237.31	234.60
	308	38.70	35.72	41.48	43.61	237.21	234.70
	318	41.17	38.11			237.50	234.82
Cu ²⁺	298	37.36	34.60			240.36	231.95
	308	39.80	36.88	41.48	41.48	240.47	231.83
	318	42.24	39.31			240.57	232.15
Zn ²⁺	298	37.99	34.85			245.51	245.70
	308	40.51	37.43	42.54	45.74	245.71	245.79
	318	42.97	39.84			245.71	245.91
Cd ²⁺	298	39.00	35.60			232.40	228.50
	308	41.35	37.85	37.23	39.35	232.48	228.40
	318	43.71	40.24			232.58	228.70
Hg ²⁺	298	39.43	36.17			233.71	230.24
	308	41.74	38.44	37.23	39.35	233.63	230.14
	318	44.17	40.84			233.90	230.43

Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , and Hg^{2+} (i.e., the stability constants increase with increasing temperature).¹⁹

2. The negative values of ΔG for the complexation process of Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , and Hg^{2+} with VA and PVA suggest the spontaneous nature of such process.
3. The ΔH values are positive for the complexation process of VA and PVA with Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , and Hg^{2+} . This means that these processes are endothermic and favorable at higher temperatures.²⁰
4. The positive values of ΔS for the complexation process of VA and PVA with Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , and Hg^{2+} confirm that the complex formation is entropically favorable.

References

1. Morlay, C.; Cromer, M.; Mougnot, Y.; Vittori, O. *Talanta* 1998, 45, 1177; 1999, 48, 1159.
2. Al-Sarawy, A. A. *Portug Electrochim Acta* 2001, 19, 99.
3. El-Bindary, A. A.; El-Sonbati, A. Z.; El-Deeb, N. A. *J Appl Polym Sci* 2000, 77, 2552.
4. Marinsky, J. A.; Reddy, M. M. *Org Geochem* 1984, 7, 207.
5. Benegas, J. C.; Cleven, R. F. M.; Van den Hoop, A. G. T. *Anal Chim Acta* 1998, 369, 109.
6. Cesaro, A.; Paoletti, S.; Urbani, R.; Benegas, J. C. *Int J Biol Macromol* 1989, 11, 66.
7. Jeffery, G. H.; Bassett, J.; Mendham, J.; Denney, R. C. *Vogel's Textbook of Quantitative Chemical Analysis*, 5th ed.; Longman: London, 1989.
8. El-Sherbiny, M. F.; Al-Sarawy, A. A.; El-Bindary, A. A. *Boll Chim Farmac-Anno* 2002, 141, 274.
9. Al-Sarawy, A. A. *Chem Pap* 2003, to appear.
10. Elvira, C.; Roman, J. S. *Polymer* 1997, 38, 4743.
11. Irving, H.; Rossotti, H. S. *J Chem Soc* 1954, 2904.
12. Irving, H.; Rossotti, H. S. *J Chem Soc* 1953, 3397.
13. Rossotti, F. I. C.; Rossotti, H. S. *Acta Chem Scand* 1955, 9, 1166.
14. Beck, M. T.; Nagybal, I. *Chemistry of Complex Equilibria*; Wiley: New York, 1990.
15. Bebot-Bringaud, A.; Dange, C.; Fauconnier, N.; Gérard, C. *J Inorg Biochem* 1999, 75, 71.
16. Merce, A. L. R.; Szpoganicz, B.; Khan, N. A.; Do Thanh, X.; Bouet, G. *J Inorg Biochem* 1999, 73, 167.
17. Mailk, W. U.; Tuli, G. D.; Madan, R. D. *Selected Topics in Inorganic Chemistry*, 3rd ed.; Chand S. & Co. Ltd: New Delhi, 1948.
18. Frank, H.; Evans, L. *J Phys Chem* 1945, 13, 507.
19. El-Sonbati, A. Z.; El-Bindary, A. A.; El-Deeb, N. A. *Design Mon Polym* 2001, 4, 357.
20. El-Sonbati, A. Z.; El-Bindary, A. A.; El-Deeb, N. A. *React Funct Polym* 2002, 50, 131.