

## Simultaneous Determination of Ionization Constant, Solubility Product and Solubility for Slightly Soluble Acids and Bases. Electrolytic Constants for Abietic Acid

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The following paper presents a simple and relatively reliable method for simultaneous estimation of ionization constant, solubility product and solubility of the undissociated molecules of slightly soluble weak acids or bases from a single potentiometric titration. As an example results for abietic acid are presented.

The idea of the method is to carry out a titration (performed with a strong titrator) starting from the range where the weak electrolyte is completely ionized and extend it over the flocculation point. From the first part of the curve the ionization constant is calculated, from the later part the solubility product. The solubility of the undissociated molecules is then obtained by dividing these two constants. A rough estimation of this intrinsic solubility can also be obtained from the equilibrium pH value where flocculation starts. The method also seems to be useful to determine the solubility of volatile weak acids and bases.

It is true that with decreasing solubility only a small part of the neutralization curve becomes useful for calculation of the ionization constant. Nevertheless the method seems to be as accurate for relatively insoluble weak acids and bases as the usual method, based on pH measurements of their salts at different concentrations. The accuracy of the method last mentioned is more influenced by omnipresent carbon dioxide especially at low concentrations, and in many cases formation of association ions at higher concentrations will limit the range of useful concentrations.

In the following the method is applied to monobasic acids, but can easily be extended to other cases.

*Theory.* The equations are derived for the acid HA dissolved in an excess of a strong base and titrated with a strong acid. Using common symbols, where  $C_a$  stands for the total concentration of weak acid  $HA + A^-$ , and  $C_s$  for the concentration of excess titrator added after the neutralization point,  $pK_s$  is calculated from

$$pK_s = pH + \log \frac{C_s + C_{OH^-} - C_{H_3O^+}}{C_a - C_s + C_{H_3O^+} - C_{OH^-}} + \frac{0.5 \sqrt{\mu}}{1 + \sqrt{\mu}} \quad (1)$$

After flocculation  $pK_L$  is computed from

$$pK_L = pK_s - \log a_{HA} = pH - \log (C_a + C_{H_3O^+} - C_s - C_{OH^-}) + \frac{0.5 \sqrt{\mu}}{1 + \sqrt{\mu}} \quad (2)$$

The solubility of the undissociated molecules  $L_{HA}$  is  $= \frac{K_L}{K_s}$

At the point of beginning flocculation we obtain

$$L_{HA} = C_s + C_{OH^-} - C_{H_3O^+} \quad (3)$$

At higher concentrations the solubility of the undissociated acid  $L_{HA}$  can be reached already at the neutralization point. This salt concentration  $C'_a$  is determined by the equation

$$C'_a \approx C_{A^-} = \frac{K_s \cdot C_{HA} \cdot C_{OH^-}}{K_w} = \frac{K_s \cdot C_{HA}^2}{K_w} = \frac{K_s \cdot L_{HA}^2}{K_w} \quad (4)$$

#### Application to abietic acid

Abietic acid was isolated from American rosin (grade WW) principally according to Palkin and Harris<sup>1</sup>. 600 g rosin was dissolved in 500 ml ethanol and boiled with 5 ml concentrated hydrochloric acid and 1 g hydroquinone for half an hour. The abietic acid crystallized slowly on cooling. The acid was recrystallized as n-butylamine salt from benzene. After two recrystallizations 125 g of the salt was obtained as a faintly yellow product. The salt is relatively stable to oxidation and can be stored. The pure acid was prepared by dispersing the salt in ethyl ether, and crystallizing the free acid twice from acetone after decomposition of the salt with hydrochloric acid. Abietic acid was finally obtained in about 4 mm large colourless crystals, with a melting point of 168°—172°C, and an optical activity  $\alpha_D = -103.8$  to  $-105.1^\circ/\text{dm}$  at 20°C in ethanol. The acid was vacuum dried and can be stored in vacuum and darkness for some days. Traces of oxidation products can be removed by recrystallization from acetone. All abietic acid used for the experiments described here was freshly prepared.

2.8—3.0 g abietic acid was dissolved at 90°—95° C in 0.2 *N* sodium hydroxide (about 10 % excess) under nitrogen atmosphere. Dissolving was complete in 10 minutes and after dilution to 500 ml a nearly colourless solution ( $\sim 0.02$  *N*) was obtained. Electrometric titrations were carried out on 150 ml portions of this solution in a nitrogen stream at  $20^\circ \pm 1^\circ$  C with 0.002 *N* hydrochloric acid during vigorous stirring. A Beckman low alkali error glass electrode (no. E 11903), a standard calomel reference electrode and an electronic potentiometer (Radiometer PHM3f) were used. The system was calibrated by a borate buffer according to Natl. Bur. Standards<sup>2</sup>. No correction for liquid junction potential has been applied. The liquid junction of the reference electrode was cleaned by letting out some KCl solution before each pH measurement. This was necessary because sometimes abietic acid was salted out at the liquid junction. The titration was extended over the flocculation point, which was observed. After measuring several points in the region of distinct precipitation the dispersion was retitrated with 0.02 *N* NaOH. The use of a dilute acid titrator was necessary to make sure of rapid equilibrium in the surroundings of the flocculation point. Activity coefficients were estimated according to equation (1) and (2). The  $pK_w$  value of Harned and Hamer<sup>3</sup> was used for the calculations.

Abietate solutions show the characteristic phenomena of long chain electrolytes<sup>4</sup>. A critical concentration of 0.015 *N* is obtained from conductivity measurements. Anomalies in the hydrolysis curve and formation of association ions are not observed until about this critical concentration<sup>4,5</sup>. The electrolytic constants are obtained from measurements below this concentration.

It is impossible to exclude small amounts of carbon dioxide. Further the acid is slowly oxidized. Both the carbonic acid and the oxidation products of abietic acid are stronger acids than abietic acid. Consequently they cause a decrease in the amount of titrator acid required to reach the first neutralization point from the alkaline side. Knowing the amount of all other electrolytes, it is possible to calculate the amount of interfering acids from the observed neutralization point. The first ionization constant of carbonic acid is about 15 times larger than that of abietic acid. Consequently only a slight amount of the bicarbonate ion is titrated in the first part of the neutralization. Thus this part will be most useful for accurate calculations. However, even then the contaminations show up as a slight upward trend in the  $pK_s$  value and downward trend in the  $pK_L$  value.

This is exemplified in Table I which shows the results of a complete titration (the last part carried out with a more concentrated titrator). Using the mean values of  $pK_s$  and  $pK_L$  obtained from this titration (7.55 and 11.41 respectively), a theoretical titration curve is calculated for comparison.

Table 1. Titration of sodium abietate with hydrochloric acid.

0.93445 g HAB in 15.00 ml 0.2046 N NaOH diluted to 150 ml.

Titration with 0.001994 N resp. 0.01994 N HCl.

Standard borax buffer; 0.01 N borax, 0.02 N NaCl (pH 9.20) gives - 77.8 mV.

ml HCl added	EMF observed mV	Calculated constants		EMF calculated mV <sup>z</sup>
0.00 *	- 197.9			- 189.5
25.00	- 185.2			- 182.7
40.0	- 176.7			- 174.2
50.0	- 168.8			- 167.7
60.0	- 158.8			- 158.5
70.0	- 148.3			- 150.7
80.0	- 134.4			- 133.3
90.0	- 118.9			- 119.6
92.5 †	- 113.7	pK <sub>s</sub>	7.47	- 112.1
95.0	- 109.6	»	7.55	- 109.6
100.0	- 100.8	»	7.57	- 99.5
105.0	- 96.0	»	7.62	- 91.3
110.0 ††	- 93.1	L <sub>HA</sub>	1.54 10 <sup>-4</sup>	- 85.8
120.0	- 90.5	pK <sub>L</sub>	11.48	- 86.7
145.0	- 86.6	»	11.49	- 84.4
5.0 **	- 84.8	»	11.44	- 83.4
10.5	- 82.4	»	11.42	- 82.4
20.5	- 78.5	»	11.41	- 78.5
30.5	- 75.0	»	11.41	- 75.0
40.5	- 71.2	»	11.40	- 71.0
50.5	- 67.0	»	11.39	- 67.9
75.5	- 53.7		11.35	- 57.4
100.5	- 33.5		(11.26)	- 41.8
110.5	- 19.1			- 33.2
115.5	- 8.2		(10.82)	- 26.1
117.5	- 2.6			- 23.5
119.5	+ 4.9			- 20.2
121.5	+ 14.9			- 16.4
123.5	+ 28.0			- 11.8
125.5	+ 48.0		(10.48)	- 6.6
127.5	+ 73.8			- 0.0
129.5	+ 104.8			+ 9.1
131.5	+ 155.0			+ 23.1
133.5	+ 201.7			+ 55.8
135.5	+ 225.2			+ 208.0
137.5	+ 238.2			+ 236.3
139.5	+ 246.2			+ 244.1
149.5	+ 272.1			+ 270.8
174.5	+ 293.8			+ 293.8

\* 0.001994 N HCl. \*\* 0.01994 N HCl. † Neutralization point. †† Opalescens. <sup>z</sup> From constants in preceding column.

The agreement is good in the alkaline branch. In the acid branch the deviations are larger because the contaminating acids are titrated simultaneously with the abietic acid. In the test 2.782 milliequivalents abietate were added, but another 0.103 milliequivalents of acid were found from the position of the first equivalence point. At the second equivalence point another 0.056 milliequivalents had interfered.

Table 2 shows the average values of the electrolytic constants obtained in eight titration experiments.

Table 2. Electrolytic constants for abietic acid at 20° C.

Experiment	$pK_s$	$pK_L$	Intrinsic solubility $L_{HA}$	
			Calculated from $L_{HA} = K_L/K_s$	Observed at flocculation point
A I	$7.69 \pm 0.00$	$11.37 \pm 0.03$	$2.1 \cdot 10^{-4}$	$L < 1.3 \cdot 10^{-4}$
A II		$11.37 \pm 0.02$		$L < 1.3 \cdot 10^{-4}$
A III	$7.88 \pm 0.01$	$11.36 \pm 0.02$	$3.3 \cdot 10^{-4}$	
B I	$7.68 \pm 0.04$	$11.40 \pm 0.02$	$1.9 \cdot 10^{-4}$	$L < 1.1 \cdot 10^{-4}$
B I retitr.	$7.43 \pm 0.06$	$11.41 \pm 0.04$	$1.0 \cdot 10^{-4}$	$0.5 < L$
B II	$7.66 \pm 0.07$	$11.41 \pm 0.02$	$1.8 \cdot 10^{-4}$	$L < 1.0 \cdot 10^{-4}$
B II retitr.	$7.79 \pm 0.01$	$11.42 \pm 0.03$	$2.3 \cdot 10^{-4}$	$0.6 < L < 1.3 \cdot 10^{-4}$
C I	$7.54 \pm 0.07$	$11.45 \pm 0.02$	$1.2 \cdot 10^{-4}$	
C I retitr.	$7.55 \pm 0.05$	$11.46 \pm 0.05$	$1.2 \cdot 10^{-4}$	$0.4 < L < 0.8 \cdot 10^{-4}$
C II	$7.51 \pm 0.09$	$11.43 \pm 0.01$	$1.2 \cdot 10^{-4}$	$L < 1.0 \cdot 10^{-4}$
C II retitr.	$7.55 \pm 0.03$	$11.46 \pm 0.03$	$1.2 \cdot 10^{-4}$	$0.4 < L < 0.6 \cdot 10^{-4}$
D (table 1)	$7.55 \pm 0.03$	$11.41 \pm 0.02$	$1.4 \cdot 10^{-4}$	$L < 1.5 \cdot 10^{-4}$
Mean value	$7.62 \pm 0.04$	$11.41 \pm 0.01$	$(1.6 \pm 0.3) \cdot 10^{-4}$	$0.5 < L < 1.0 \cdot 10^{-4}$

The value for  $K_L$  and  $K_s$  are in good agreement. From what has been said earlier it could not be supposed that the value of  $L_{HA}$  calculated from  $K_L$  and  $K_s$  should coincide with that obtained from observation of commencing flocculation, in fact it is amazing that the results agree so well. The accuracy of the constants obtained is further influenced by liquid junction potentials, uncertainty in assumed activity factors, etc. The authors estimate the accuracy to be represented by

$$\begin{aligned}
 pK_s &= 7.6 \pm 0.2 \\
 pK_L &= 11.4 \pm 0.1 \\
 L_{HA} &= (1.6 \pm 1.0) \cdot 10^{-4} \text{ moles/l}
 \end{aligned}$$

Ekwall and Lindström <sup>4</sup> in a preliminary study, using crude acid, obtained as an upper limit  $K_s L_{\text{HA}} = K_L = 1.19 \cdot 10^{-11}$  in reasonable agreement with our lower value on pure abietic acid  $3.7 \cdot 10^{-12}$ . In various works on paper sizing the ionization constant of rosin acids has been assumed to be between  $10^{-4}$  and  $10^{-11}$ .

#### SUMMARY

For slightly soluble acids and bases the ionization constant, solubility product and solubility can be determined by a single potentiometric titration. The method was applied to abietic acid and the values thus obtained are  $pK_s = 7.6 \pm 0.2$ ,  $pK_L = 11.4 \pm 0.1$  and the solubility of undissociated molecules  $L_{\text{HA}} = (1.6 \pm 1) \cdot 10^{-4}$  moles/l.

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