

The Ionization Constant, Solubility Product and Solubility of Abietic and Dehydroabietic Acid

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The ionization constant (K_s), solubility product (K_L) and solubility in water of abietic and dehydroabietic acid at 20°C have been determined simultaneously from potentiometric titrations of their aqueous salt solutions within soap concentrations ranging from below the concentration of limited ion association to above the critical concentration for micelle formation resulting in:

For abietic acid: $pK_s = 6.4$; $pK_L = 11.3$ and L , the solubility of unionized acid: $= 1.2 \times 10^{-5}$ mole/litre.

For dehydroabietic acid: $pK_s = 5.7$; $pK_L = 10.5$ and $L = 1.62 \times 10^{-5}$ mole/litre. Total solubilities at 20°C are presented as a function of pH.

True ionization constants can be determined only below the concentration of limited ion association. This concentration of limited ion association for these acids was estimated from the ionization data.

As our measurements on lauric and myristic acid¹ and those of Ekwall² on bile acids have shown that a true ionization constant has to be determined below the limited concentration of ion association, it was decided to re-investigate data of Back and Steenberg³ on the electrolytic constants of abietic acid. Dehydroabietic acid was then included in this investigation as it has been indicated that this acid is significantly stronger and more water soluble^{4,5}.

The method of Back and Steenberg for simultaneous evaluation of the ionization constant, the solubility product and the solubility of the unionized protolyte from single potentiometric titrations has been employed.

EXPERIMENTAL

High purity abietic acid ($[\alpha]_D^{20} = -105.5^\circ$) was prepared by recrystallization as butylamine abietate as described earlier³. Dehydroabietic acid of at least 98 % purity ($[\alpha]_D^{20} = 63.0^\circ$) was kindly provided by Hercules Powder Co. The experiments were carried out using the equipment and experimental technique described in the paper on lauric and myristic acid¹, which may be referred to for details. In order to obtain a rapid dissolution of resin acid crystals, sodium resinate solutions for potentiometric titrations had to be prepared with a sodium hydroxide excess of about 10 %.

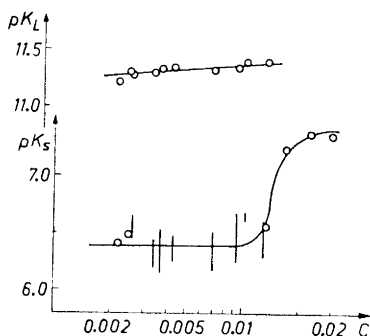


Fig. 1. pK_s and pK_L of abietic acid at 20°C as a function of the total resinate and resin acid concentration, C , in mole/litre at the neutralization point.

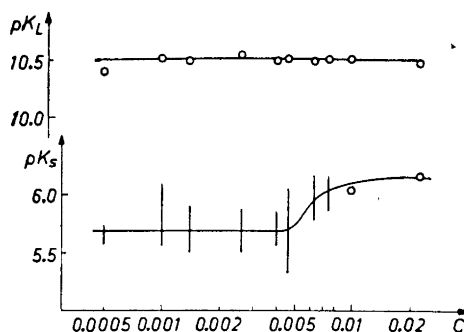


Fig. 2. pK_s and pK_L of dehydroabietic acid at 20°C as a function of the total resinate and resin acid concentration, C , in mole/litre at the neutralization point.

RESULTS

The ionization constant, K_s , the solubility product, K_L , and the solubility of unionized acid, L , were all calculated from single potentiometric titrations and corrected for activity coefficients as earlier described^{1,3}. If, due to formation of micelles or associated ions, the presumptions made in these calculations are not valid, the constants calculated naturally represent pseudo-constants only, probably of little interest.

Ionization constants

The ionization constants of abietic and dehydroabietic acid, calculated from the measurements performed, are presented as pK_s values in the lower part of Figs. 1 and 2 as a function of the total resinate and resin acid concentration at the neutralization point. Where necessary, the range of pK_s values within each single titration is indicated by a line.

In agreement with the results obtained for fatty acids¹ and bile acids² the data for abietic acid and dehydroabietic acid show true concentration independent ionization constants to be obtained at low resinate concentrations only. The mean values, given together with their 90% confidence limits, are at 20°C

for abietic acid: $pK_s = 6.4 \pm 0.1$ (6.39 ± 0.08)

$$K_s = 4.1 \times 10^{-7} \text{ mole/litre (} 3.4 \times 10^{-7} \text{ to } 4.9 \times 10^{-7} \text{)}$$

for dehydroabietic acid: $pK_s = 5.7 \pm 0.1$ (5.71 ± 0.05)

$$K_s = 2.0 \times 10^{-6} \text{ mole/litre (} 1.7 \times 10^{-6} \text{ to } 2.2 \times 10^{-6} \text{)}$$

Bruun⁵ from monolayer measurements obtained a pK_s value for dehydroabietic acid of 5.84 in good agreement with these direct measurements.

At higher resinate concentrations a pseudo-ionization constant is obtained because of ion association and following micelle formation, not accountable for in evaluating the primary data¹. Thus, as is seen from Figs 1 and 2 the apparent pK_s value is increasing within a certain concentration range, dominated by limited ion association. Unfortunately the measurements of Back and Steenberg³ on the ionization constant of abietic acid were carried out within this intermediate concentration range, not accounting for the then little known occurrence of ion association below the critical concentration for micelle formation.

As was also shown for fatty acids¹ and bile acids², the pseudo-constant levels off to a constant value, after ion association has reached the stage of micelle formation. Thus, the data of Figs. 1 and 2 permit an estimation of the concentration at which limited ion association becomes obvious, namely

for the abietate anion	10^{-2} mole/litre
for the dehydroabietate anion	6×10^{-3} »

Solubility

The solubility products obtained for abietic and dehydroabietic acid are plotted in the upper part of Figs. 1 and 2 as pK_L values against the total resinate and resin acid concentration at the neutralization point. In both cases the pK_L value obtained can be regarded as independent of concentration (although for abietic acid a very slight change of pK_L with concentration shows up). Also, as pointed out for fatty acids, constant pK_L values occurred, once the acid had coagulated within the system. The following mean solubility products with their 90 % confidence ranges are obtained

for abietic acid	11.31 ± 0.03
for dehydroabietic acid	10.50 ± 0.03

Back and Steenberg earlier obtained within a limited concentration range the pK_L value of 11.4, in reasonable agreement with these data.

The solubility of unionized acids, L , obtained as the quotient of the solubility product and corresponding ionization constant^{1,3}, given with its 90 % confidence limits, is at 20°C

for abietic acid	1.2×10^{-5} mole/litre	(0.9×10^{-5} to 1.6×10^{-5})
	3.6 mg/litre	(3 to 5 mg/litre)
for dehydroabietic acid	1.6×10^{-5} mole/litre	(1.4×10^{-5} to 2.0×10^{-5})
	4.9 mg/litre	(4 to 6 mg/litre)

The total solubility, *i.e.* the sum of the solubilities of ionized and unionized acid at 20°C, determined by L and K_L , respectively, is presented in Fig. 3 as a function of pH. At the equivalence point defined by $a_{H_3O^+} = a_{A^-}$, *i.e.* in a saturated water solution, the mean total solubilities are at 20°C

for abietic acid	1.4×10^{-5} mole/litre = 4.3 mg/litre
for dehydroabietic acid	2.2×10^{-5} mole/litre = 6.6 mg/litre

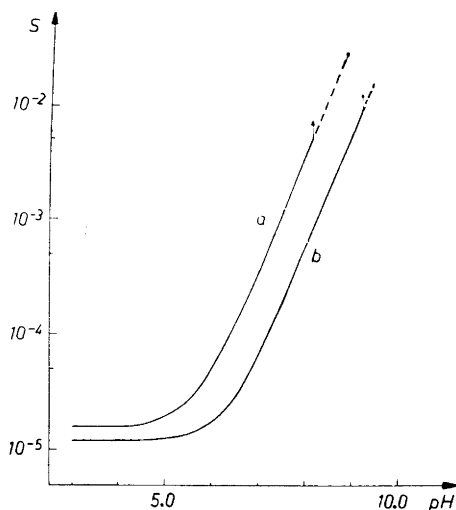


Fig. 3. Total solubility, S , in mole/litre as a function of pH for a) abietic acid b) dehydroabietic acid.

Obviously there is a significant difference in the total solubility of abietic and dehydroabietic acid, which has already found technical applications in the separation of resin acids by fractional acidification⁴. Solubility data, as here presented, make possible more detailed calculations on the efficiency of such a separation.

The solubility curves of Fig. 3 are valid only until the concentration of limited ion association has been reached. Thereafter, the true total solubility might exceed the one to be calculated. In Fig. 3 the corresponding point in the curve is indicated by an arrow. In the following part of the curves calculated dashed lines have been employed to indicate a minimum solubility. The curves are discontinued at a pH-value, where for available anions the critical concentration of micelle formation has been reached. Above this concentration, due to formation of mixed resin acid — resinate ion micelles, a rather rapid increase in total resin acid solubility will occur.

It might be pointed out that in mixtures of several resin acids or of resin and fatty acids the apparent solubility effects mentioned above will all occur at still lower single resinate anion concentrations because of the formation of mixed resinate and soap anion micelles⁶, and of mixed associated ions.

Abietic acid *versus* dehydroabietic acid

The differences in solubility between abietic and dehydroabietic acid are in the direction expected. Dehydroabietic acid containing an aromatic ring is more hydrophilic and more water soluble than abietic acid containing a conjugated double bond only. The significant increase in ionization constant

occurring on aromatization of this B-ring (containing the *isopropyl*group) might be due to steric effects.

Differences obviously also occur in ion association and micelle formation. The ratio of the true ionization constant to the pseudo-constant after micelle formation is considerably larger for abietic acid than for dehydroabietic acid, while limited ion association occurs within a more narrow concentration range. Such differences in micelle formation have also been indicated in the work of Corrin, Klevens and Harkins⁷.

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