The colloidal pK_a of lipophilic extractives commonly found in *Pinus radiata*

DOUGLAS S. McLEAN*†, DAVID VERCOE*, KAREN R. STACK‡ AND DES RICHARDSON§

SUMMARY

This paper uses established experimental methods to determine the colloidal pK_a values for a variety of weak organic acids found in the lipophilic extractives of *Pinus radiata* at 20°C and 50°C.

The 50°C colloidal pK_a values, to the knowledge of the authors, are published for the first time in this paper. This data will hopefully lead to a better understanding of how these weak organic acids interact in the 50°C temperature range of modern pulp and papermaking.

The colloidal pK_a values for behenic, lignoceric and cerotic acids are also believed to be published for the first time in this paper.

Keywords

Colloidal pK_a, resin acids, fatty acids, wood pitch, *Pinus radiata*, behenic acid, lignoceric acid, cerotic acid

When a carboxylic acid (RCOOH) is placed in water it undergoes dissociation to form the hydronium ion (H_3O^+) and its conjugate base (RCOO⁻). This reaction can be written as:

$$RCOOH + H_2O \rightleftharpoons H_3O^+ + RCOO^- \quad [1]$$

Generally chemists like to represent this equation by an equilibrium constant (K), which is defined as:

$$K = \frac{[H_3O^+][RCOO^-]}{[RCOOH][H_2O]} \quad [2]$$

In most bench scale laboratory experiments the concentration of water, $[H_2O]$, is relatively constant. Thus the equilibrium constant can be redefined as an acidity constant (K_a). This is written as follows:

$$K_a = \frac{[H_3O^+][RCOO^-]}{[RCOOH]} \quad [3]$$

* PhD Student,
† Corresponding author,
‡ Research Fellow,
  Pulp and Paper Research Group, School of Chemistry, University of Tasmania, Private Bag 75, Hobart, Tasmania 7001.
§ Senior Specialist Process Chemistry,
  Research & Development Australasia, Norske Skog Paper Mills (Australia) Ltd, Boyer, Tasmania 7140.

The negative logarithm of each side of the Equation 3 yields Equation 4.

$$-\log K_a = -\log[H_3O^+] - \log\left(\frac{[RCOO^-]}{[RCOOH]}\right) \quad [4]$$

The terms: and are given special names. These are pK_a and pH respectively and are expressed as:

$$pK_a = -\log K_a \text{ and } pH = -\log[H_3O^+] \quad [5, 6]$$

By substituting these definitions into Equation 4 we derive the Henderson-Hasselbach equation:

$$pK_a = pH - \log\left(\frac{[RCOO^-]}{[RCOOH]}\right) \quad [7]$$

When 50% of the acid is ionised (or dissociated):

$$[RCOO^-] = [RCOOH] \quad [8]$$

As a result of the above case (Equation 8) the second half of Equation 7 is eliminated, as the negative logarithm of 1 equals 0.

$$-\log\left(\frac{[RCOO^-]}{[RCOOH]}\right) = -\log\left(\frac{1}{1}\right) = 0 \quad [9]$$

Equation 7 thus becomes:

$$pK_a = pH \quad [10]$$

In order to determine the pK_a of a given organic acid one must determine the pH at which 50% of the acid is ionised, or dissociated. This can be determined by titrating the organic acid with a base. The pH at which half of the volume (V) of base used to reach the equilibrium point (ep) is the value of the pK_a for that acid (Fig. 1).

This procedure does not work for acids that are insoluble in water. Many of the organic acids that papermakers are interested in have a limited solubility. For acids that are not soluble in water, the general procedure is to form the salt, by adding a base. The salt is then back titrated with an acid (1).

The relationship between pK_a and pH is important for papermakers in order to understand the chemistry of the system

and the nature of the species that are present. Effluent pH in relation to the pK_a of the acidic lipophilic extractives of softwoods has an influence on their biodegradation (2) and the subsequent effluent toxicity (3,4). The pH of pulp and papermaking process waters has an influence on the deposition of these acidic lipophilic extractives onto pulp and papermaking surfaces in the form of pitch (5,6). The interaction of these extractives varies with pH (7).

Kanicky and Shah (8) found that the pK_a values for fatty acids, as determined by acid-base titration, is dependent on the chain length of the fatty acid and also the concentration. They attributed the effects to molecular association of the chemical species, even below critical micelle concentration (CMC). They were able to demonstrate that extrapolation of the pK_a to very dilute concentrations of ~5x10⁻¹¹ M yielded a pK_a close to 5.0 for the fatty acids they investigated (C6 to C12 fatty acid chain length). In addition Kanicky and Shah (8) showed that once the fatty acid concentration was above its CMC the pK_a of the fatty acid became constant. As a result the term 'colloidal pK_a' is introduced in this paper to describe the pK_a of solutions of fatty and resin acids above their CMC.

This paper focuses on determining the colloidal pK_a of the various acidic lipophilic extractives in *P. radiata*. *P. radiata* was selected due to its importance to the pulp and paper industries of Australia and New Zealand (9). The weak organic acids examined in this paper were selected from the lipophilic extractive analytical works conducted on *P. radiata* by others (10-12). These compounds consisted primarily of saturated and unsaturated fatty acids with chain lengths of 12 to 26 carbon atoms and the eight resin acids. The pK_a for some of these compounds have been determined previously by others (1,13-21) at 20°C though some discrepancy does exist between some of the values in the literature.

Measurements of behenic acid (C22:0), lignoceric acid (C24:0) and cerotic acid (C26:0) will be undertaken
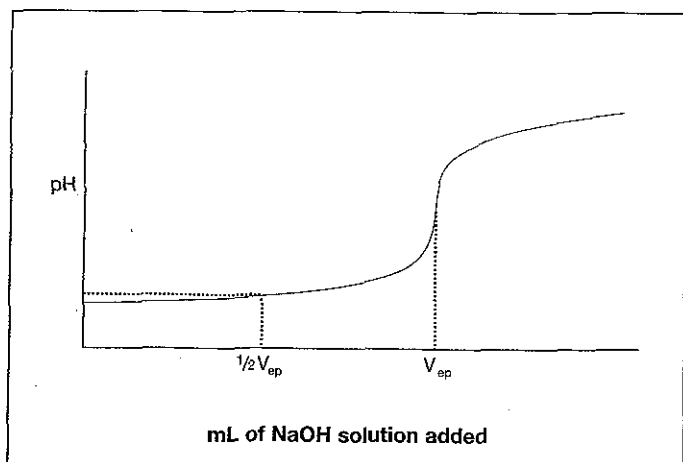
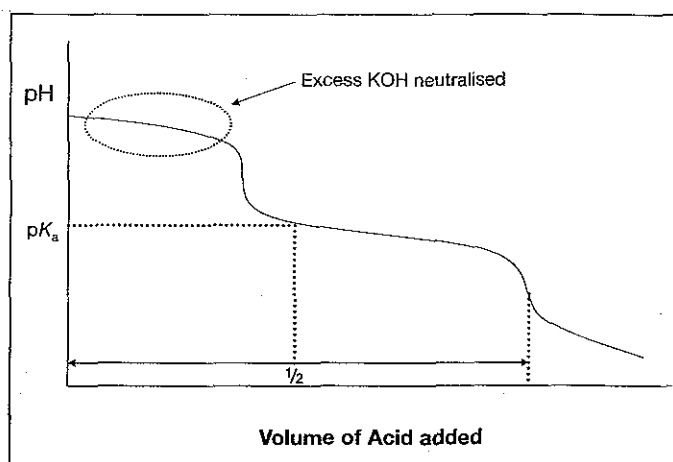Fig. 1   Titration of a weak acid with a base.

Fig. 2   pK_a for an insoluble weak organic acid.

and reported for the first time. This paper also aims to determine the colloidal pK_a of these substances at 50°C, which is a representative temperature of modern papermaking.

EXPERIMENTAL

The fatty acids were obtained from Sigma-Aldrich and had a purity of 99% or greater, with the exception of stearic acid which was 95+% purity. In order to further improve its purity the stearic acid was recrystallised in ethanol twice. The resin acids were obtained from Helix-Biotech and had a purity of 99% or greater, with the exception of abietic acid which had a purity of 90 to 95%.

The majority of the substances examined are insoluble in water. As a result, the potassium salts of the acids were first prepared using 10% molar excess of potassium hydroxide (KOH), the minimum amount of distilled water and heated at 90°C for 20 minutes. At all times the amount of acid used was above the CMC of the acid (22). The salt solution was then filtered through a 0.2 μm filter.

The potassium salts were then titrated using a weak solution (0.005 to 0.0005N) of hydrochloric acid (HCl) in order to determine the colloidal pK_a value. An average of three colloidal pK_a values and their standard deviations are reported. These methods were based on the work of others (1,8).

RESULTS AND DISCUSSION

The pK_a of some of the weak insoluble organic acids investigated in this paper have been reported in the literature (1,8,13,19). These researchers have determined the pK_a as the pH at which half the volume of acid required to titrate the salt formed from the addition of excess base. Figure 2 shows the typical s-shaped curve that is obtained. The first part of the curve can be attributed to neutralisation of the excess base present when forming the soluble salt. In order to ensure only one inflection point, some of the researchers prepared solutions such that there was no excess potassium hydroxide.

In order to ensure that the pK_a determined by this method of titrating the salt

with acid yields the same pK_a when the acid is titrated with base as shown in Figure 1, measurements were made using acetic acid. Treating the acetic acid as an insoluble acid, which it is not, the salt was first formed by adding 10% molar excess of KOH. This salt was then titrated using a weak solution of HCl. A graphic representation of this titration is shown in Figure 3.

The pK_a determined by this method was found to be 4.77 +/- 0.09 (point A) which is in close agreement with the well known pK_a, at 20°C, of 4.74 (23). This confirms that the method is acceptable.

There were two difficulties in reproducibility of these acid-base titrations of the insoluble weak organic acids. The first difficulty was ensuring that the potassium salt of the acids had been formed. If too little KOH were added, not all of the acid would have been converted to the potassium salt. If too much KOH is added the time required for the titration is increased, due to the volume of HCl added to neutralise the excess KOH concentration [OH-]. This increased titration time
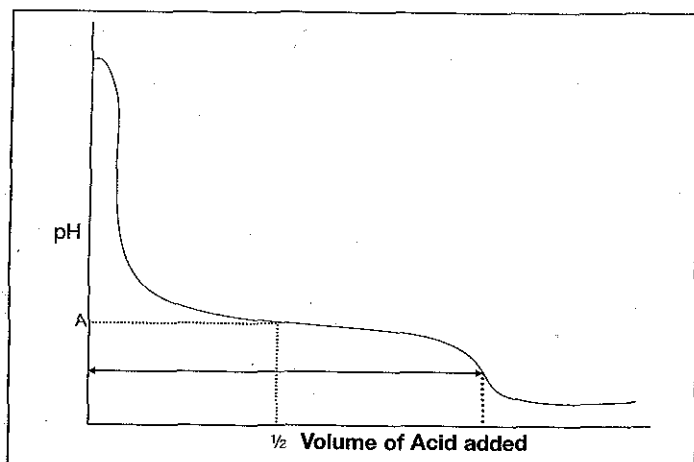

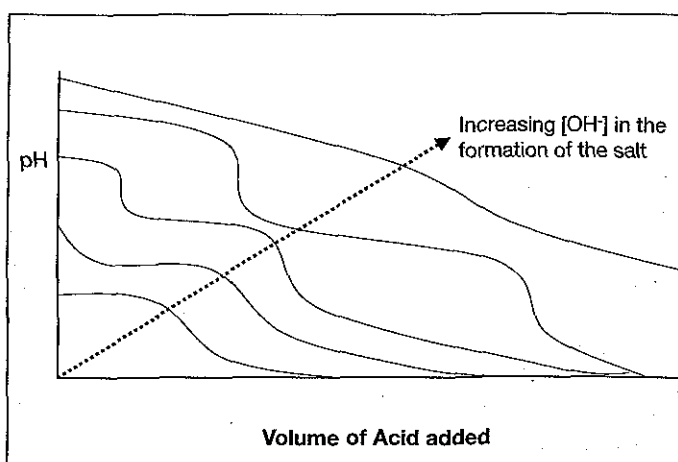Fig. 3   pK_a of acetic acid, treated as an insoluble acid.

Fig. 4   Titration curves with increasing molar ratio of KOH to that of the analyte acid.

elongates the curves to the point where determining the two inflection points is quite difficult. This problem is shown in Figure 4.

In order to correct the problem found with high KOH concentrations one would increase the titrating acid's (HCl) concentration $[H_3O^+]$. The second problem in regards to reproducibility occurs when the titrating acid concentration is too strong. With a very high acid concentration only one inflection point is observed, as one decreases the titrating acid concentration both inflection points become distinguishable. This issue is highlighted in Figure 5.

During the titrations we saw a change in the physical nature of the solutions. The photographs of what we saw are presented in Figure 6. Kanicky and Shah (13) reported similar observations.

In Figure 6 the solution became more and more cloudy from image I towards III whereas the solution gained in particulate matter from images III through V. Kanicky and Shah (13) explained image IV in terms of the formation of crystals and precipitate. Back and Steenberg (1) referred to image IV as the flocculation point. Langmuir made very similar observations on many of the same fatty acids, though he was looking at surface tension instead of pH (24). Rayleigh (25) and Dupré (26) noted difficulty in understanding the phenomena associated with Figure 6. These solutions contain a mixture of free molecules, associated molecules, micelles and colloids. The colloidal nature of the solutions is obvious from the visual observations and based on the work by Kanicky (21), the pK_a that is being measured is a pK_a of the colloids and not the true molecular pK_a. Colloidal stability is of particular importance to the pulp and paper industry, as it relates to pitch deposition (27,28). Further work is needed in order to understand the colloidal formation and colloid stability of the solutions and the effect pH is having, particularly why the colloidal pK_a is so much higher than the molecular pK_a.

A summary of the colloidal pK_a values determined is presented in Table 1. The reason that colloidal pK_a was examined rather than 'molecular pK_a' is that the authors believe that the colloidal pK_a is more relevant to papermakers as the acid concentrations usually found in the papermaking waters, are above ~5x10^{11} M (8). Supporting this decision to use colloidal

pK_a rather than molecular pK_a is work by Suckling et al. (29) that showed the pH at which resin components were soluble in water correspond with colloidal pK_a values reported in Table 1. Additionally work by Sundberg et al. (30) showed the pH at which colloidal resin droplets were dissolved into the water phase correspond to the colloidal pK_a values reported in Table 1.

Figure 7 shows that as fatty acid chain length increases so does colloidal pK_a (8). The shorter chain length (C1:0 to C9:0) fatty acids have a pK_a values between 4 to 5. There is a critical chain length somewhere between 9 and 12 carbons where the colloidal pK_a starts to trend upwards on a steeper slope with increasing chain length. The increase in colloidal pK_a
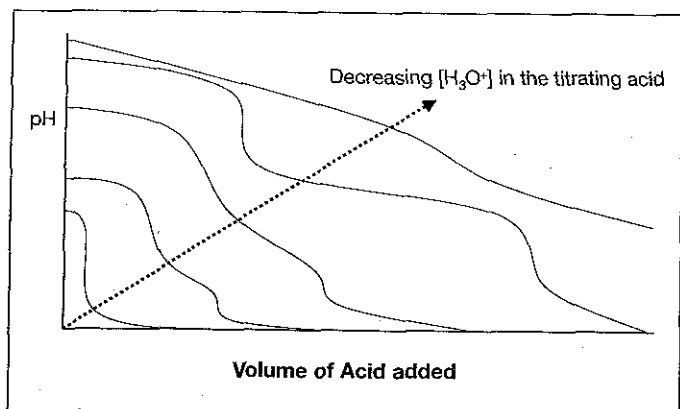
Table 1
The colloidal pK_a values of lipophilic extractives commonly found in *Pinus radiata*. (STD denotes two sigma standard deviation).

	pK$_a$ @20°C	STD @20°C	pK$_a$ @50°C	STD @50°C
Saturated fatty acids				
Lauric (C12:0)	7.07 5.3[a] ~7.5[b]	0.04	6.48	0.34
Myristic (C14:0)	7.88 ~6.3[a] 8.1-8.2[b] 7.9[c]	0.11	7.25	0.35
Palmitic (C16:0)	8.34 5.06[d] 8.6-8.8[b] 9.7[c]	0.44	8.63	0.32
Stearic (C18:0)	9.89 10.15[e] 9.0[f]	0.43	9.28	0.43
Arachidic (C20:0)	9.82	0.27	9.28	0.17
Behenic (C22:0)	9.89	0.63	9.53	0.19
Lignoceric (C24:0)	10.21	0.1	9.81	0.15
Cerotic (C26:0)	10.21	0.09	9.83	0.12
Unsaturated fatty acids				
Elaidic (18:1;(trans)9)	8.31 9.95[e] 8.3[c]	0.03	7.65	0.24
Oleic (18:1;(cis)9)	8.22 5.02[d] 9.85[e]	0.35	8.29	0.07
Linoleic (18:2;(cis)9,12)	7.43 9.24[e] 8.0[c]	0.25	7.79	0.13
Linolenic (18:3;(cis)9,12,15)	6.83 8.28[e]	0.03	6.26	0.06
Resin acids				
Abietic	7.26 7.6[g] 6.39[h] 7.15[i]	0.11 0.2[g] 0.08[h]	6.18	0.04
Dehydroabietic	6.77 5.84[j] 5.71[h] 7.25[i]	0.15 0.05[h]	6.18	0.07
Isopimaric	7.08	0.09	6.23	0.01
Neoabietic	7.07	0.01	6.23	0.14

a=Ref.15, b=Ref.19, c=Ref.21, d=Ref.18, e=Ref.13, f=Ref.20, g=Ref.1, h=Ref.16, i=Ref.17, j=Ref.14

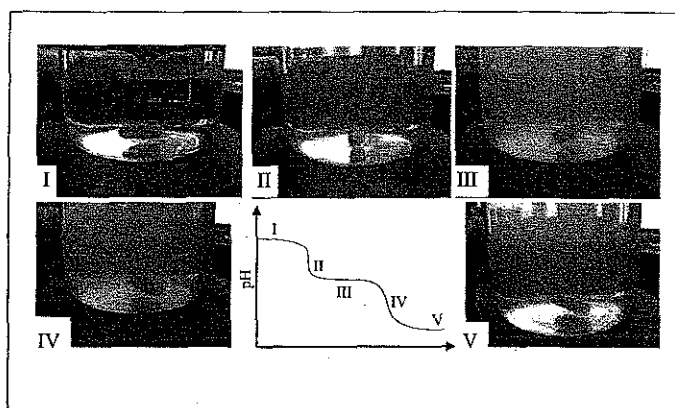**Fig. 5** Titration curves with decreasing molarity of the titrating acid (HCl).

Fig. 6 Photographs from the titration of lauric acid. (Similar observations were made for each acid studied).

values starts to taper off to about 10 when the fatty acids have 18 or more carbon atoms in their straight chain. This is an interesting result as it indicates that the higher chain length fatty acids have a colloidal pK_a that is basic (i.e. above 7). Further work is needed to explain this.

The effect of degree of saturation of the fatty acid in relation to colloidal pK_a shows that, as degree of unsaturation increases, the colloidal pK_a decreases at 20°C. A similar result was observed by Kanicky and Shah (13). The effect is less clearly demonstrated at 50°C due to experimental errors.

The colloidal pK_a of resin acids was found to be between 6 and 7. The trends would appear to be driven by the electron-withdrawing groups present in the various resin acid structures. Of the four resin acid structures shown in Figure 8, dehydroabietic acid's aromatic ring is the strongest electron-withdrawing group. Consequently dehydroabietic acid has the lowest colloidal pK_a value at 20°C. The double bonds in neoabietic and isopimaric

acids are further away from the acidic proton than the double bonds of abietic acid. Due to this greater withdrawal distance the colloidal pK_a values for neoabietic and isopimaric acids are lower than the colloidal pK_a value for abietic acid at 20°C. It is unclear why abietic acid does not follow the electron-withdrawing group interpretation at 50°C.

Taking standard deviation and experimental error into account the colloidal pK_a values are slightly lower at 50°C than at 20°C. These temperature biased colloidal pK_a values are expected given the inverse relationship between pK_a and temperature in the thermodynamic definition of pK_a, shown in Equation 11.

$$pK_a = \frac{\Delta G_{aq}}{\ln 10 \cdot RT} \qquad [11]$$

Where: R is the gas constant
T is temperature in Kelvin
ΔG_{aq} is the Gibbs energy of the acid in an aqueous solution.

This result of the colloidal pK_a values being lower at 50°C than at 20°C is important for papermakers in predicting the type of species present at a particular pH and hence the colloidal behaviour and deposition tendency of the extractives.

CONCLUSIONS

Measurements of the colloidal pK_a values for insoluble fatty acids and resin acids found in *P. radiata* have been determined at 20°C and 50°C using a method that converts the insoluble acids to their corresponding soluble salts by adding a slight excess of base and then titrating with acid. The values at 20°C are higher than those values expected for pK_a of short chain weak acids. Values are reported for behenic acid and lignoceric acid and cerotic acid for the first time.

The values that have been determined in this paper are reported as a colloidal pK_a as the solutions investigated are in a colloidal state being above their CMC. The colloidal nature of the species present
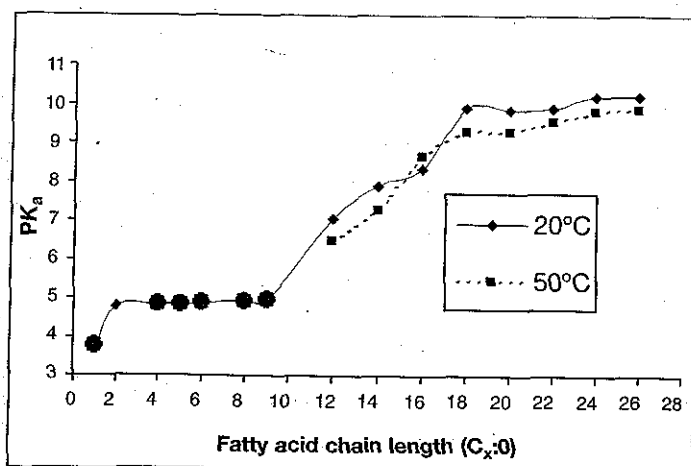

Fig. 7 Fatty acid chain length versus colloidal pK_a. (Circles (●) denote literature pK_a values (31), diamonds (♦) 20°C and squares (■) 50°C denote experimental colloidal pK_a values.)
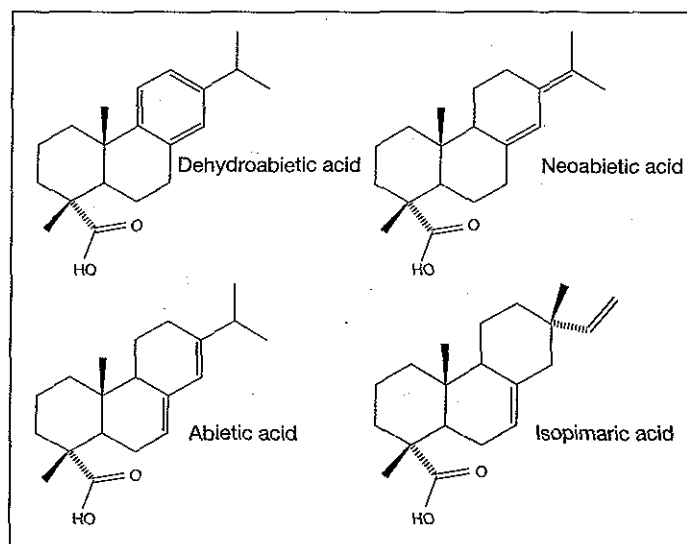

Fig. 8 Resin acid structures.

appears to be affecting the values determined. Further work is planned in order to understand how the colloidal properties affect the measured pK_a.

The colloidal pK_a values determined for the fatty acids show that the values are significantly higher than the typical molecular pK_a values for weak acids ($pK_a = 4$-5) and higher still as the chain length increases and the degree of saturation increases. Above C18 the colloidal pK_a values of higher chain length fatty acids reach a constant value of about 10. The resin acids have colloidal pK_a values between 6 and 7 and the trends can be explained by the differences in electron-withdrawing groups present.

The colloidal pK_a values were found to be lower at 50°C. This can be explained through thermodynamics.

ACKNOWLEDGEMENTS

REFERENCES

(1) Back, E. and Steenberg, B. – Simultaneous determination of ionization constant, solubility product and solubility for slightly soluble acids and bases. Electrolytic constants for abietic acid, *Acta Chem. Scand.* 4:810 (1950).

(2) Werker, A.G. and Hall, E.R. – The influence of pH on the growth-linked biodegradation kinetics of selected resin acids found in pulp mill effluent, *TAPPI J.* 82(7):169 (1999).

(3) McLeay, D.J., Walden, C.C. and Munro, J.R – Influence of dilution water on the toxicity of kraft pulp and paper mill effluent. Including mechanisms of effect, *Water Res.* 13:151 (1979).

(4) Leach, J.M. and Thakore, A.N. – Identification of the constituents of kraft pulping effluent that are toxic to juvenile Coho salmon (*Oncorhynchus kisutch*), *J. Fish. Res. Board Can.* 30(4):479 (1973).

(5) Dreisbach, D.D. and Michalopoulos, D.L. – Understanding the behavior of pitch in pulp and paper mills, *Tappi J.* 72(6):129 (1989).

(6) Allen, L.H. – The importance of pH in controlling metal-soap deposition, *Tappi J.* 71(1):61 (1988).

(7) McLean, D.S. – **The effect of wood extractive composition on pitch deposition, MSc Thesis** ,School of Chemistry, University of Tasmania, Hobart, p.106 (2003).

(8) Kanicky, J.R. and Shah, D.O. – Effect of premicellar aggregation on pKa of fatty acid soap solutions, *Langmuir* 19(6): 2034 (2003).

(9) Uprichard, J.M. – Introduction to chapter 1, **Pulp and Paper from Radiata Pine**, Appita and Forest Research, Carlton, p.2 (2002).

(10) McDonald, I.R.C. and Porter, L.J. – Resin and fatty acid composition of *Pinus radiata* whole wood, and its relation to the yield and composition of New Zealand tall oil, *N. Z. Jl Sci.* 12(2):352 (1969).

(11) Suckling, I.D., Gallagher, S.S. and Ede, R.M. – A new method for softwood extractives analysis using high performance liquid chromatography, *Holzforschung* 44(5):339 (1990).

(12) Wallis, A.F.A. and Wearne, R.H. – Characterisation of resin in radiata pine woods, bisulfite pulps and mill pitch samples, *Appita J.* 50:409 (1997).

(13) Kanicky, J.R. and Shah, D.O – Effect of degree, type, and position of unsaturation on the pK(a) of long-chain fatty acids, J. *Colloid Interface Sci.* 256(1):201 (2002).

(14) Bruun, H. – An interpretation of the effect of ionization upon monolayer properties of rosin acids, *Acta Chem. Scand.* 6:955 (1952).

(15) Nyrén, V. and Back, E. – The ionization constant, solubility product and solubility of lauric and myristic acid, *Acta Chem. Scand.* 12(6):1305 (1958).

(16) Nyrén, V. and Back, E. – The ionization constant, solubility product and solubility of abietic and dehydroabietic acid, *Acta Chem. Scand.* 12(7):1516 (1958).

(17) Tolstikov, G.A., Irismetov, M.P., Andrusenko, A.A. and Goryaev, M.I. – Synthetic transformation of resin acids III. The effect of the conformation transfer and dissociation constants of diterpene acids, *Izv. Nats. Akad. Nauk Resp. Kaz. Ser. Khim.* 18:71 (1968).

(18) White, J.R. – Dissociation constants of higher alkyl phosphate esters, phosphonic acids, phosphonous acids, phosphinic acids and carboxylic acids, *J. Am. Chem. Soc.* 72:1859 (1950).

(19) Kanicky, J.R., Poniatowski, A.F., Mehta, N.R. and Shah, D.O. – Cooperativity among molecules at interfaces in relation to various technological processes: Effect of chain length on pK_a of fatty acid salt solutions, *Langmuir* 16(1):172 (2000).

(20) Christodoulou, A.P. and Rosano, H.L. – Effect of pH and nature of monovalent cations on surface isotherms of saturated C_{16} to C_{22} soap monolayers, *Adv. Chem. Ser.* 84:210 (1968).

(21) Heikkila, R.E., Deamer, D.W. and Cornell, D.G. – Solution of fatty acids from monolayers spread at the air-water interface: Identification of phase transformations and the estimation of surface charge, *J. Lipid Res.* 11(3):195 (1970).

(22) Vercoe, D., Stack, K., Blackman, A., Yates, B. and Richardson, D. – An innovative approach to characterising the interactions leading to wood pitch deposition., *J. Wood Chem. Technol.* 24(2): In press (2004).

(23) Windholz, M. – The Merck Index, Merck & Co., Inc., Rahway, N.J., U.S.A. (1983).

(24) Langmuir, I. – The constitution and fundamental properties of solids and liquids. Part II. Liquids, *J. Am. Chem. Soc.* 39(9): 1848 (1917).

(25) Rayleigh, L. – On the tension of recently formed liquid surfaces, *Proc. R. Soc. London A* 47: 281 (1890).

(26) Dupré, A. – Théorie méchanique de la chaleur, Gauthier-Villars, Paris, p.484 (1869).

(27) Sihvonen, A.L., Sundberg, K., Sundberg, A. and Holmbom, B. – Stability and deposition tendency of colloidal wood resin, *Nord. Pulp Pap. Res. J.* 13(1):64 (1998).

(28) Garver, T.M. and Yuan, H. – Measuring the response of pitch control strategies, *Pulp Pap. Can.* 103(9):24 (2002).

(29) Suckling, I.D., Hua, H.L. and Uprichard, J.M. – Factors affecting resin removal from radiata pine mechanical pulps, *Appita J.* 43(3):217 (1990).

(30) Sundberg, K., Pettersson, C., Eckerman, C. and Holmbom, B. – Preparation and properties of a model dispersion of colloidal wood resin from Norway spruce, *J. Pulp Pap. Sci.* 22(7):J 248 (1996).

(31) Lide, D.R. – **CRC handbook of chemistry and physics**, CRC Press, New York (1999).