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Thermometric Titration of Shellac Solution

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The thermometric titration method has been adopted for determining the acid values of shellac and its components in non-aqueous medium. The values obtained compare well with those reported in literature. The values of heat of neutralization in alcohol have also been determined.

SEVERAL methods, such as alkalimetric, potentiometric and the iodometric methods, are available for the determination of the acid value of lac. However, all these methods suffer from certain drawbacks. In the alkalimetric method, it is difficult to determine the correct end point while titrating dark coloured lac solutions. The potentiometric method is difficult to adopt in general practice, involving, as it does, costly instruments. The iodometric method invariably gives low values[1]. The thermometric method[2] has now been tried, because in this method the colour of lac is not an impediment, and no costly equipment is needed. Subsequently, the heat of neutralization has also been determined, as this characteristic constant does not appear to have been reported in literature so far.

Acid value — The determination of acid value was carried out in a cylindrical pyrex Dewar flask (int. diam., 4 cm; height, 20 cm) fitted with a cork with holes for inserting a Beckmann thermometer, stirrer and burette. The method was first standardized against a pure colourless acid, aleuritic acid (a derivative of shellac), using a standard solution of alcoholic potassium hydroxide. The acid value obtained from the volume-temperature curve was in close agreement with that obtained by the conventional alkalimetric titration using phenolphthalein as indicator.

TABLE 1 — ACID VALUES OF DIFFERENT MATERIALS

(The values are averages of 3-4 determinations)

Material	Acid value	
	Exp. value	Lit. value
Aleuritic acid	184·4	184·5 (theoretical)
Seedlac	79·9	—
Shellac	72·2	65-75
Bleached lac (BRF)	79·5	73-118
Platina shellac	72·4	65-75
Hard lac resin	63·7	55-60
Soft lac resin	110·2	103-110

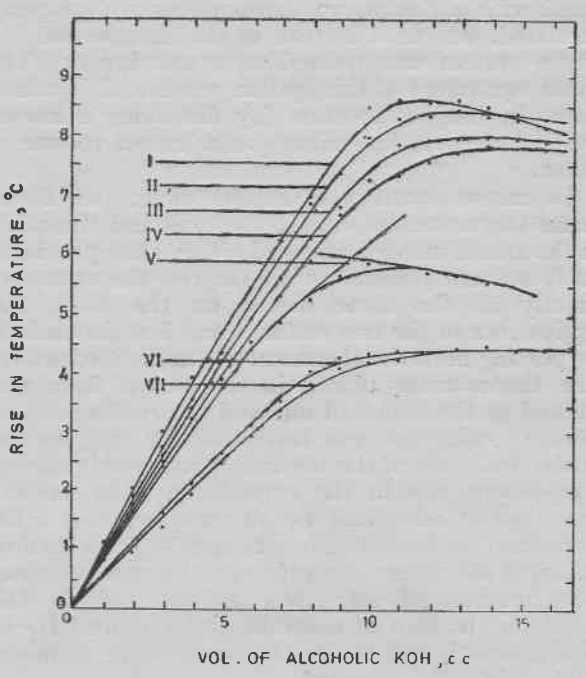

Fig. 1 — Rise in temperature on titrating lac and shellac solutions against alcoholic KOH [(I) Aleuritic acid (1·5217 g); (II) bleached lac BRF (3·756 g); (III) Platina shellac (4·1703 g); (IV) soft lac resin (2·4074 g); (V) seedlac (3·259 g); (VI) shellac (3·5017 g); and (VII) hard lac resin (3·7359 g)]

The lac sample was ground to pass through a 30 mesh sieve and a weighed quantity (2-4 g) was dissolved in neutral rectified spirit (100 ml). The solution was then transferred to a Dewar flask. It was slowly and steadily stirred and its temperature noted in a Beckmann thermometer every half a minute. After steady state had been attained, 0·5*N* alcoholic potassium hydroxide solution was added from a burette in 1 ml lots at 1 min intervals and the temperature in the Beckmann thermometer noted. The addition of alkali was continued till the temperature started dropping. From the plot between the rise in temperature and the volume of the alcoholic alkali added (Fig. 1), the volume of alkali required to just neutralize the lac solution was read and the acid value calculated as usual. The results are given in Table 1. It is

seen that the values obtained agree closely with those obtained by earlier workers employing the conventional method[3].

No sharp break is perceptible in any of the plots in Fig. 1 and they all bend smoothly in the neutralization zones. This indicates that during titration, apart from neutralization, no other possible reactions, such as the formation of complex salt or decomposition, take place.

Heat of neutralization — The apparatus used for this purpose was the same as the one used for acid value determination, except that a separating funnel, fitted with a Beckmann thermometer and properly insulated, was used instead of the burette and the whole system was treated as a calorimeter. The water equivalent of this system was first determined from the heat of solution (by dissolving a known weight) of potassium nitrate in a known volume of water.

To ensure accuracy of measurement, two Beckmann thermometers, one in the acid and the other in the alkali, marked acid and alkali, were provided. As it was not possible to set the two thermometers exactly at the same degree on the scale, the equivalence of the two readings was first determined by putting both the thermometers in distilled water. The thermometer placed in the Dewar flask was treated as the standard one and the reading of the other thermometer was corrected according to the initial difference of the two and subsequently during temperature rise in the experiment. The method was then standardized by titrating aqueous 0·1*N* potassium hydroxide solution against 0·1*N* hydrochloric acid. The temperatures of the two solutions were maintained very close to each other. The value for the heat of neutralization obtained (13·45 kcal g mole^{-1}) was nearly the same as the standard value (13·7 kcal g mole^{-1}).

For determining the heat of neutralization of shellac, a weighed quantity of dried powdered sample (9-10 g) was dissolved in 100 ml ethyl alcohol and the solution transferred to the Dewar flask. The temperature of the solution indicated by the acid thermometer was noted at half minute interval till the temperature was stable. A known volume of 0·1*N* alcoholic potassium hydroxide solution was taken in the separating funnel and the temperature of this solution indicated by the alkali thermometer was recorded at the same intervals. When the temperature in both the solutions was steady, the alkali was added rapidly into the flask with efficient stirring and the readings in the acid thermometer recorded. The two thermometer readings were converted to the same scale as explained previously, taking into account the radiation correction as well. Finally, the rise in temperature was plotted against time and the difference of initial temperatures (*A-B* and *A'-B'* for two separate solutions) and the final temperatures (*C-D*) was read from the plot (Fig. 2). The average values of heat of neutralization for lac and shellac samples are given in Table 2.

The heat of neutralization of lac was calculated from the water equivalent of the system and the rise in temperature using the following equation:

$$H = W(t_3-t_1)+ms(2t_3-t_1-t_2)$$

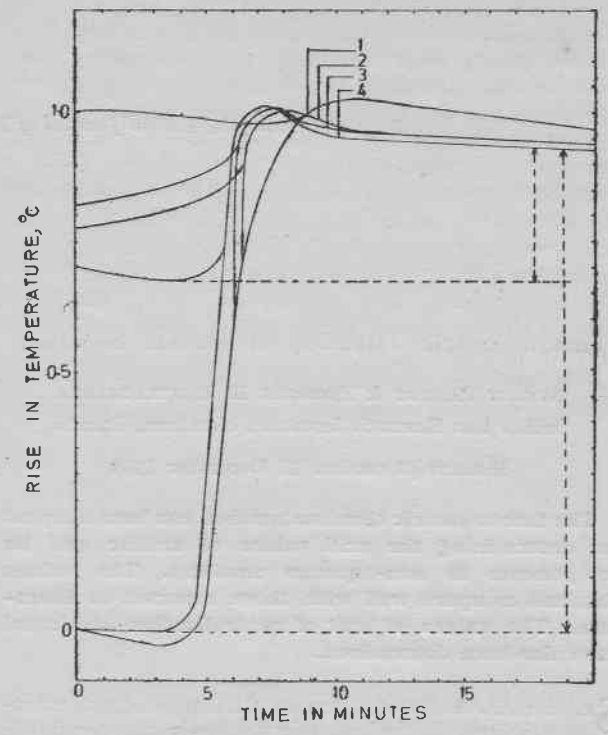

Fig. 2 — Rise in temperature of lac solution in Dewar flask at different time intervals [(1) Shellac; (2) seedlac; (3) Platina shellac; and (4) bleached lac]

Table 2 — Heats of Neutralization of Different Materials

(The values are averages of 3 determinations)

Material	Heat of neutralization kcal/g mole
Seedlac	10·35
Shellac	9·66
Platina shellac	9·55
Bleached lac	10·69

where H is the heat of neutralization of the substance (in kcal/g mole); W, the water equivalent of the Dewar flask with stirrer; m, the wt of the solution in ethyl alcohol; s, the specific heat of ethyl alcohol; t_1, the temperature of shellac solution; t_2, the temperature of potassium hydroxide solution; and t_3, the final temperature of the neutralized solution.

As the volumes of the solvent in the solutions of shellac and potassium hydroxide were the same and the heat capacities of these two dilute solutions were considered equal, the percentage of error in this case is negligible.

In Fig. 2, *A-B* and *A'-B'* indicate the initial temperatures of shellac solution and alcoholic solution of potassium hydroxide respectively. *B-B'-C* indicates the rise of temperature when potassium hydroxide is added to the shellac solution and when there is no more rise in temperature of the reaction mixture.

It is seen that *B-B'-C* is nearly parallel to the ordinate, which signifies that the reaction is very

rapid even at room temperature. The heat of neutralization of a strong acid with a strong base is 13·7 kcal g mole^{-1}. In the case of shellac, however, it was found to be 9·55-9·66 kcal g mole^{-1}, showing that the acid in this case is weak. This is in conformity with the conclusion from the ionization constant for shellac reported in literature, namely $3{\cdot}96 \times 10^{-6}$ for the free acid of shellac[4] and $4{\cdot}3 \times 10^{-6}$ for lac acid[5]. In the case of seedlac and bleached lac, the heat of neutralization was found to be slightly higher (10·35 and 10·69 kcal g mole^{-1} respectively) than that for shellac, which may be due to their higher acid values (79·9 and 79·5 respectively).

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