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DIPOLE MOMENTS OF THE CHIEF CONSTITUENTS OF LAC AND ROSIN

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ABSTRACT. Dipole moment of abietic acid, the chief constituent of rosin, has been determined from measurements on its dilute solutions in 1, 4 dioxane. Similar measurements have also been made on dilute dioxane solutions of pure lac resin (reinharz) and soft lac resin, the two main constituents of lac. The temperature of measurements was 25°C for all of them. The values obtained for the dipole moment of abietic acid, soft lac resin and pure lac resin are 1.35, 4.61 and 7.45 Debye units respectively.

INTRODUCTION

Rosin and lac are two very important natural resins. The chief constituent of rosin is abietic acid and it forms more than 90% of American rosin (Ellis, 1935). Considerable work has been done on the constitution of abietic acid by various investigators (Tschirch and Studer, 1904; Ruzicka and Meyer, 1922; Haworth, Letsky and Marvin, 1932; Bardhan and Sengupta, 1932) and there is still some minor controversy on the position of two double bonds and the carboxyl group regarding the structure proposed by Ruzicka and his co-workers (Ruzicka, Ankersmit and Frank, 1932; Ruzicka, Waldmann, Meier and Hösli, 1933). But the empirical formula $C_{20}H_{30}O_2$ for this acid has been established now. Shellac, however, has been shown to consist of two main fractions regarding its solubility in diethyl ether. The fraction which is insoluble in ether has been termed 'Reinharz' or 'Pure lac resin' or 'a-lac', and has been shown by Palit and Bhattacharya (1939) to consist entirely of a dibasic acid of molecular weight 1900. By treating this pure resin with very strong caustic alkali (5N KOH) and then decomposing the potassium salt with dilute sulphuric acid a white crystalline acid was obtained by Harries and Nagel (1922). This acid has been termed aleuritic acid and its constitution has been definitely established as 9, 10, 16 tri-hydroxy-palmitic acid by these authors. Dialysis experiments (Palit, 1939) with shellac solutions in alcohol have shown that soft resin and pure resin of lac are separate bodies and further experiments with these fractions showed that they could not be further fractionated. This fact shows that pure lac resin or soft lac resin is not a mixture of substances of varying molecular weights, as was previously considered (Verman and Bhattacharya, 1934; Shaeffer, Weinberger and Gardner, 1938; Shaeffer and Gardner, 1938), but that they are most probably homogeneous bodies. The structure of pure lac resin,

however, is not yet known but a few tentative proposals have been put forward by a few workers from time to time.

The ether-soluble fraction of shellac which is often called soft lac resin or simply 'soft resin' from its tarry consistency has been shown by Palit and Bhattacharya (1930) to consist of a monobasic acid of molecular weight 530. Subsequent work at this Institute (1940) on the constitution of this fraction of lac showed that the molecule has one hydroxyl group and one carboxyl, and probably the empirical formula is $C_{31}H_{56}O_{5}$. It is apparent therefore that these substances cannot be included in the category of those whose structures have been established beyond doubt except perhaps abietic acid. Nevertheless the object of undertaking the dielectric study of these substances lies in the search for a very satisfactory explanation of the anomalous solubility of these substances in some of the organic solvents. Palit (1940) has very recently put forward an explanation for this anomalous solubility from a study of the solubility of a few natural resins in different mixed solvents. It has been observed in that connection that many of the non-solvents for a particular resin may be rendered good solvents for the same by adding some 'polar-helpers' to those non-solvents. From the current conceptions regarding solvation of large molecules and subsequent dissolution (Sheppard, Carver and Houck, 1928; Hildebrand, 1936) it may be inferred that either the molecules of these resins are themselves polar in nature or the different constituent bodies act as polar substances towards these mixed solvents, the polar-helpers thus acting as solubilisers. The determination of dipole moments of the chief constituents of rosin and lac is therefore of considerable interest. In a previous paper the author (Bhattacharya, 1942) has reported the results of dipole measurement on aleuritic acid and its alkyl esters in dioxane. The high value of electric moment of aleuritic acid reported in that paper has given impetus to carry on the work further. But the extreme difficulty which is attendant with the purification of such resinous substances must not be under-estimated. The process of purification of abietic acid or aleuritic acid by repeated crystallisation, though laborious and very tedious, must be considered a simple matter when compared with the process of purification of the constituents of lac resin, *viz.*, pure resin and soft resin. Their purity cannot be checked by determining the melting point as is usually done in the case of crystalloids and the determination of the refractive index was also a meagre help in this matter. The elimination of other constituent bodies from a particular sample leaving only the desired fraction was the only process which was resorted to with extreme carefulness in these purification methods. •

Wilson and Wenzke's (1934) finding that the solvent 1, 4 dioxane when used for the determination of electric moments gives correct values of moments of fatty acids had led many workers to use this solvent subsequently for the same purpose. The same solvent has been used in these experiments also, and it is perhaps the only suitable solvent for lac constituents.

, PREPARATION OF MATERIALS

Dioxane.—The dioxane used in these experiments was American produce bottled by A. Boake Roberts & Co., Ltd., of England and was purified according to the method already described in a previous paper (Bhattacharya, 1942). The various physical constants of the material are as follows :

$$F.P. = 11°.6\ C, \quad n^{25} = 1.4198, \quad d^{25} = 1.0282, \quad \epsilon^{25} = 2.2024.$$

Abietic acid.—Abietic acid manufactured by J. D. Riedel—E. de Hüen A. G. of Germany was recrystallised six times from dilute methyl alcohol. After four crystallisations, the melting point of the sample became practically constant at 160°C. After two more crystallisations the sample was finally washed with the same dilute alcohol which was being used for crystallisation and it was dried in a vacuum-desiccator. Typical clusters of abietic acid crystals were obtained after a few crystallisations. The sample was then kept under vacuum to avoid oxidation.

A second sample was also used by crystallising twice from dilute methyl alcohol abietic acid obtained from American wood rosin by the method of Steele (1922). The two samples, however, gave practically the same values of polarisation.

Pure lac resin.—Pure lac resin (Reinharz) of about 92-95% purity was first prepared according to the method suggested by Palit (1942). It was powdered, mixed up with silver sand and then extracted with diethyl ether in a soxhlet apparatus for the removal of final traces of soft resin. Finally the sample was extracted with petroleum ether in the same soxhlet apparatus for the removal of any trace of shellac-wax that might have been left. The criterion of the final stages of soxhlet extraction was obtained from the complete evaporation of a few drops of the extracted liquid from a clean glass slide without leaving any stain on it. When this was achieved, the resin was dissolved in alcohol, filtered free from sand, precipitated again from a large volume of distilled water and then drawn into fibres on softening from the boiling water. These fibres were dried in air, powdered in a mortar and then finally dried in a vacuum-oven at 40°C.

Soft lac resin.—Soft lac resin was first obtained by soxhlet extraction with ether from kusmi shellac. This soft resin was then dissolved in pure ethyl acetate and boiled with decolourising charcoal to remove any colouring matter. The resin was then boiled with petroleum ether under a reflux vigorously stirring from time to time. Petroleum ether was renewed several times till this liquid evaporated on a clean glass slide without leaving a stain. The resin was then heated at 105°C in a vaccum-oven in order to free it from any adherent solvent.

4—1455P—III

EXPERIMENTAL

The experimental cell was made of pyrex glass according to the design of Sayce and Briscoe. The apparatus and the method used has been described previously (Bhattacharya, 1942).

Density measurements were made with a pyknometer of approximately 25 cc. capacity and the refractive index measurements were carried out with a Zeiss-Abbe Refractometer according to the method suggested by the author in a previous paper (Bhattacharya, 1940).

All the measurements were carried out at 25°C.

SYMBOLS

The symbols used in the equations and tables are : w, the weight fraction of the solute; d^{25}, the density of the solution at 25°C ; e, the dielectric constant of the solution. P_1, the polarisation of the solute ; P_∞, the polarisation of the solute at infinite dilution ; MR_D, the molar refraction for the sodium D-line; μ, the dipole moment; T, the absolute temperature ; p, the specific polarisation ; p_2, the specific polarisation of the solvent ; p_{12}, the specific polarisation of the mixture or solution, M_1, the molecular weight of the solute.

CALCULATIONS

Polarisations were calculated using Sugden's formula (Sugden, 1934) for specific polarisation instead of molar polarisation,

$$p = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{1}{d}.$$

The total polarisation is calculated from the relation,

$$P_1 = M_1 \left(p_2 + \frac{p_{12} - p_2}{w} \right).$$

Polarisations at infinite dilutions were obtained by employing the graphical extrapolation method using P_1—w curves.

Molar refraction for abietic acid was calculated as the sum of the atomic refractions (Swictonslawski, 1920 ; Getman, 1937) for the sodium D-line. For pure lac resin and soft resin, however, the electronic polarisations were calculated from refractive index measurements.

The contributions of the atomic polarisations to polarisations at infinite dilutions were neglected. The dipole moments were calculated from the relation,

$$\mu = .0127 \times 10^{-18} \sqrt{(P_\infty - MR_D)T} .$$

ACCURACY

Density measurements may be considered to be accurate to 0.01%, Dielectric constant values are probably accurate to 0.03%.

RESULTS

TABLE I

Dielectric constants, densities, weight fractions and polarisations
Solvent—Dioxane

Abietic acid   *Soft lac resin*   *Pure lac resin*

w	d	ϵ	P_1	w	d	ϵ	P_1	w	d	ϵ	P_1
0.000000	1.0281	2.2024	—	0.000000	1.0281	2.2024	—	0.000000	1.0281	2.2024	—
0.004012	1.0284	2 2062	126·9	0 003060	1.0283	2.2188	575	0.003310	1.0284	2.2155	1647
0.004732	1.0284	2.2065	124·2	0.006175	1.0284	2.2357	577	0.007153	1.0290	2.2308	1618
0.008193	1.0286	2.2101	127·1	0.010338	1.0286	2.2559	556	0.008824	1.0292	2.2382	1641
0.012087	1.0289	2.2143	128·5	0.015948	1.0290	2.2862	557	0.012723	1.0296	2.2569	1702
0.016954	1.0293	2.2196	129·1					0.018949	1.0301	2.2804	1652

TABLE II

Substance	n	d	$\dfrac{n^2-1}{n^2+2}\dfrac{M}{d}$
Pure resin ...	1.5240	1.172	495
Soft resin ...	1.4950	1.107	137

TABLE III

| Substance	MR_D	P_α	$\mu \times 10^{18}$
Abietic acid ...	88.7	126.7	1.35
Soft lac resin ...	137	580	4.61
Pure lac resin ...	495	1650	7.45

DISCUSSION

For abietic acid the molecular weight is 302, but no such exact figure is available for either pure resin or soft resin since the composition is not yet definitely known. But actual determination of the molecular weight both by the Rast method as well as by the F.P. method using dioxane (Bhattacharya and Sen, 1939) has yielded an average value of 1900 for pure resin and 520 for soft resin. These values have been taken in these experiments. For abietic acid the molar refraction was obtained from the constituent atomic refractions corresponding to the sodium D-line, taking the Ruzicka structure. Controversy on the position of the two double bonds or the carboxyl group, however, would not affect the value of its molar refraction at all. For pure resin and soft resin, however, the molar refraction has actually been determined from refractive index and density measurements. Density of pure resin has been determined to be 1.172 and of soft resin 1.107.

The value of moment obtained for abietic acid is only 1.35 Debye units. The structure of this acid as given by Ruzicka and his co-workers is as follows:
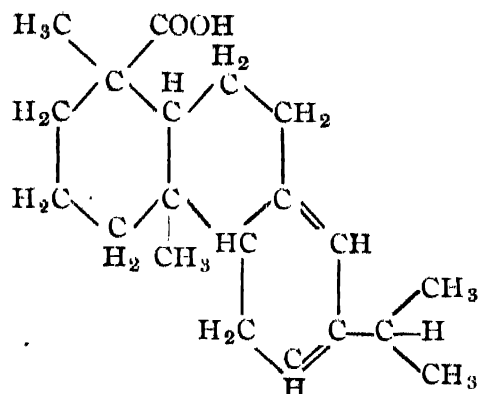
It is difficult to comment on the low value of dipole moment of abietic acid from its complex structure when so many unknown factors are present and to try to do so will be wild speculation. But we may reasonably assume from this value of moment and the formula $(CH_3)_2CH(CH_3)_2C_{14}H_{16}COOH$ that here the acid group provides the dipole. We are only concerned with the value of moment for the present.

Soft lac resin has given a value of 4.61 Debye units. Work at this Institute (1940) has revealed that a molecule of this resin contains one free hydroxyl, one free carboxyl, one lactone group and one double bond. The position of this hydroxyl or the carboxyl has not yet been finally ascertained but a tentative structure has been reported as follows :—
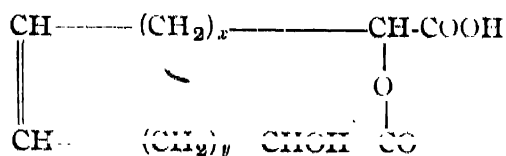
where $x + y = 25$.

This structure gives 508 as the value of the molecular weight of soft resin, but for want of sufficient evidence, the average value obtained experimentally for soft resin, *viz.* 520, has been used. This uncertainty in the molecular weight values of pure and soft resins of lac will naturally make corresponding variation in the dipole moment values but that variation will probably remain within the limits of experimental error.

Pure resin of lac has been found to have a moment of 7.45 Debye units. Its constitution is still unknown but as has already been said on saponification with very strong caustic alkali it yields aleuritic acid whose constitution is now known. Harries and Nagel (1922) reported the isolation of another acid from pure resin which they named shellolic acid and to which they ascribed the empirical formula $C_{15}H_{20}O_6$. Research workers in India, England and America, however, failed to isolate this acid. Harries and Nagel consider that the resinous

character of pure lac resin owes its origin to the splitting off of water from the molecules of aleuritic acid and shellolic acid forming lactides. Nothing more is known about the constitution of pure resin up till now.

Shellac as such was not used for the study of its dipole moment since shellac may be looked upon as a solid solution of pure resin in soft resin in the unimolecular proportion. This view may be arrived at from the following considerations:

(1) A simple alcoholic solution of shellac may be separated into its constituents, *viz.*, soft resin and pure resin, by dialysis. If shellac had been a homogeneous chemical compound this separation by such a simple physical process might not have been possible.

(2) Shellac can easily be separated into its constituents by simple extraction with solvents such as moist ether, ethyl acetate, etc.

(3) Average 'molecular weight' of shellac (if such a term is justified in the case of a mixture) as determined by Rast method using camphor or by the F. P. method using dioxane lies within 1000-1100, whereas pure resin and soft resin gives about 1900 and 520 respectively. It is also known that shellac contains about 70% of its weight of pure resin and 30% soft resin. Combining these two facts we can easily see that pure resin and soft resin are simply mixed up to form shellac. Thus, in one gm. of shellac, there are $\frac{0.7}{1900}$ gm. mol. of pure resin and $\frac{0.3}{520}$ gm. mol. of soft resin. That is, one gm. of shellac contains in all $\frac{0.7}{1900} + \frac{0.3}{520}$ gm. mol., or $\frac{934}{988} \times 10^{-3}$ gm. mol., if the individual molecules are in an uncombined state. The average 'molecular weight' of shellac, therefore, comes to be $\frac{988}{934} \times 10^3$ or 1058, *i.e.* 1060, say. The experimentally determined value for shellac also corresponds to near about this figure. The determination of dipole moment of shellac was therefore not undertaken as it is considered that its behaviour towards a solvent may be understood from the behaviour of its constituents.

It should be clearly understood, however, that polarity alone cannot give an idea of the intermolecular forces when a solute is placed inside a solvent, but that solvation is more probable when both the solute and the solvent are polar than when they are non-polar or even when one is polar and the other is not. For a better understanding of the dissolution phenomena of large molecules Coltof (1937) has recently shown that three actions, *viz.*, swelling, dispersion and ballast action of the solvents must be clearly understood. Even the same solvent behaves differently with different solutes. He thinks that the atomic groups in the solvent and solute molecules are responsible for this behaviour and a complete understanding of the behaviour of a large number of solvents towards a particular solute may lead to the making up of mixtures of non-solvents which are good

solvents of the same solute. Polarity is certainly a very important factor in this behaviour, but any one physical constant such as dielectric constant, polarisability or the electric moment cannot be the only criterion for its solubility. The fact remains, however, that pure lac resin is more polar than the soft resin and that the polarity of abietic acid is of the order of a simple fatty acid.

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REFERENCES

Bardhan, J. C., and Sengupta, S. C., 1932, Resin acids, Part II Synthesis of retene *J.C.S.*, 2798.

Bhattacharya, G. N., 1940, A Note on the Refractive Index of Shellac, *Ind. J. Phys.*, **14**, 237; 1942, Dipole Moments of Palmitic Acid, Aleuritic Acid and Alkyl Esters of Aleuritic Acid, *Ind. J. Phys.*, **16**, 369.

Bhattacharya, G. N., and Sen, H. K., 1939, Dioxane as Cryoscopic Solvent for Shellac, *Proc. Ind. Sci. Cong.*, Part III, 100.

Coltof, W., 1937, Solubility Properties of some Highly Polymeric Substances, *Jour. Soc. Chem. Ind. (Trans.)*, **56**, 363.

Ellis, C., 1935, Abietic Acid, *The Chemistry of Synthetic Resins* (Reinhold Pub. Corp.), Vol. 1, 764.

Getman, F. H., 1937, Specific and Molar Refractions, *Outlines of Theoretical Chemistry*, 86.

Harries, C., and Nagel, W., 1922, Aleuritic Acid, *Chem. Umschau.*, **29**, 135, and *Chem. Soc. Abs.*, **122** (i) 522, *Wiss. Veröffent Siemens—Konzern*, 1, 178, Untersuchungen über die Schellolsäure, *Ber. der. Deut. Chem. Ges.*, **55** B, 3833.

Haworth, R. D., Letsky, B. M., and Marvin, C. R., 1932, Syntheses of Alkylphenanthrenes, *J. C. S.*, 1784.

Hildebrand, J. H., 1936, Polarity, *Solubility*. Chap. IV, 77.

Indian Lac Research Institute, 1938, Constitution of Shellac, *Annual Report*, 3, 1940, Constitution of lac-soft Resin, *Annual Report*, 5.

Nagel, W., 1927, Untersuchungen über die Natur des Schellacks : die Konstitution der Aleuritinsäure, *Ber. der. Deut. Chem. Ges.*, **60**, 605.

Palit, S. R., 1940, Physical Chemistry of Resin Solution, Part II, Nature of Resin Solutions in Organic Solvents, *Jour. Ind. Chem. Soc.*, **17**, 537 ; Physical Chemistry of Resin Solutions, Part I, Anomalous Solubility of Shellac and other Resins in Organic Solvents, *Jour. Ind. Chem. Soc.*, **17**, 308; 1942, A Simple Method for the Preparation of Pure Lac Resin, *Jour. Ind. Chem. Soc. Ind. and New Edn.*, **8**, 25.

Palit, S. R., and Bhattacharya, G. N., 1939, A Note on the Basicity and Molecular Weight of Shellac, *J. Ind. Chem. Soc.*, **16**, 258.

Ruzicka, L., and Meyer, J., 1922, Higher Terpene Derivatives, Part II, Abietic Acid, *Helv. Chim. Acta*, **5**, 315, and *Amer. Chem. Abs.*, **16**, 2500.

Ruzicka, L., Ankersmit, P. J , and Frank, B., 1942, Polyterpenes and Polyterpenoids, LXXIII, *Helv. Chim Acta*, **15**, 1289.

Ruzicka, L., Waldmann, H., Meier, P J , and Hösli, H., 1933, Polyterpenes and Polyterpenoids, LXXVIII, Position of the Carboxyl and Double Bond in Abietic Acid *Helv. Chim. Acta*, **16**, 169.

Shaeffer, B. B., Weinberger, H., and Gardner, W. H., 1938, Nature and Constitution of Shellac, Part XIII, *Ind. Eng. Chem.*, **30**, 451.

Shaeffer, B. B., and Gardner, W. H., 1938, Nature and Constitution of Shellac, Part XII, *Ind. Eng. Chem.*, **30**, 333.

Sheppard, S. E., Carver, E. K., and Houck, R. C., 1928, Plasticity and Solvation of Cellulose Esters, *Colloid Symposium Monograph*, Vol. 5, 243.

Steele, L. L., 1922, Abietic Acid and Certain Metal Abietates, *Jour. Amer. Chem. Soc.*, **44**, 1333.

Sugden S., 1934, The Dielectric Behaviour of Dipole Substances, General Discussions, *Trans. Farad. Soc.*, **30**, 720

Swietonslawski, W., 1920, Atomic Refractions, *Jour. Amer. Chem. Soc.*, **42**, 1945.

Tschirch. A , and Studer B., 1904, American Colophony, *J. C. S* , **86** (i), 79

Verman, L. Bhattacharya, R , 1934, Isolation of Pure Lac Resin, *Lond. Shel. Res. Bur. Tech. Paper*, **1**, 9.

Wilson, C J., and Wenzke, H. H., 1934, Dipole Moment of Higher Fatty Acids, *Jour. Chem. Phys.*, **2**, 546.