ULTRASONIC STUDY OF ASSOCIATION IN DICARBOXYLIC ACIDS

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ABSTRACT

Using Jacobson's free length theory, association factors in dicarboxylic acids have been calculated. For this purpose ultrasonic velocities and temperature coefficients of velocity of six acids in the homologous series are measured, using the composite ultrasonic interferometer designed in this laboratory. It is found that these acids obey Lagemann's rule, when association is taken into account.

THE ultrasonic behaviour of monocarboxylic acids has been reported earlier in a series of communications[1-3] from this laboratory and these studies are now extended to the homologous series of dicarboxylic acids with a view to studying the similarities and differences, if any, between these two groups of substances. Interesting results are obtained and several peculiar differences exist between monocarboxylic and dicarboxylic acids in their ultrasonic behaviour. Some of the important results are reported in this communication.

The temperature variation of ultrasonic velocity and density of these acids are shown in Figs. 1 and 2 respectively and their temperature coefficients are given in column 4 of Table I. The density of the dicarboxylic acids is found to decrease with increase in molecular weight, a behaviour similar to that of normal fatty acids[3]. The ultrasonic velocity decreases and temperature coefficient of velocity increases with increasing molecular weight in dicarboxylic acids, while the opposite is the behaviour in monocarboxylic acids[1] where velocity

TABLE I

Acid	Molecular weight	Melting point* (°C)	$-\Delta c/\Delta t$ [m/sec/°C]	$C_{170°C}$ (m/sec)	$\rho_{170°C}$ (gm/cc)
Glutaric Acid ..	132·11	97·5	2·402	1169	1·150
Adipic Acid ..	146·14	151·0	2·442	1147	1·088
Pimelic Acid ..	160·17	103	2·472	1121	1·049
Suberic Acid ..	174·19	140	2·491	1102	1·014
Azalaic Acid ..	188·22	106·5	2·506	1090	0·983
Sebacic Acid ..	202·25	133	2·517	1082	0·961

* Values are taken from *Hand Book of Chemistry and Physics* (1959) (Chemical Rubber Publishing Company, Cleveland, Ohio).

A composite ultrasonic interferometer[4] is used for determining ultrasonic velocities and temperature coefficients of velocity of six dicarboxylic acids, namely, glutaric, adipic, pimelic, suberic, azalaic and sebacic acids. As all the acids have high melting points (as shown in column 3 of Table I) the ultrasonic cell is kept in a special oil bath, whose temperature is regulated within $\pm$ 0·3° C by a mercury regulator, designed in this laboratory. The whole experimental set-up is well shielded to attain thermal equilibrium. As all the substances are either Reidell or B.D.H. samples of 'Analar' purity, no further purification is attempted. The velocities and their temperature coefficients are accurate to 1 in 1000. The densities are determined correct to the third decimal place, employing a specially designed dilatometer, which records changes in volume with temperature of a known mass of the substance,

increases and temperature coefficient of velocity decreases. The magnitude of $(\Delta c/\Delta t)$ is smaller than that of monocarboxylic group of acids[1].

Using the free length theory of Jacobson[5], association factors of these acids have been calculated at 170° C, at which temperature, all of them are in the liquid state. According to Jacobson, the intermolecular free length (L_f') in liquids is related to the adiabatic compressibility (β_{ad}) by the relation

$$L_f'^2 = K^2 \cdot \beta_{ad} \qquad (1)$$

where K is a temperature dependent constant. The values of K at different temperatures upto 50° C have been given by Jacobson[5]. Wada[6] found that K is proportional to $T^{\frac{1}{3}}$ where T is the temperature in absolute degrees and that $(K/T^{\frac{1}{3}})$ is equal to a value of 36, with a variation of 1% in the temperature range 0° C to 50° C. Subsequently, Swamy[7]

TABLE II

| Acid	$V_{170°C}$ (cc)	V_0 (cc)	$L_f \times 10^8$ (cm)	$\beta_{ad} \times 10^{12}$ (at 170° C [cm²/dyne]	$L_f' \times 10^1$ (cm)	x	$[xM]^{1/2} \triangle c/\triangle t$ [gm$^{1/2}$.m. sec^{-1} °C^{-1}]
Glutaric acid ..	114·87	95·10	0·4647	63·65	0·6046	2·191	40·83
Adipic acid ..	134·28	109·6	0·5277	69·93	0·6339	1·732	38·83
Pimalic acid ..	152·72	124·1	0·5634	75·87	0·6603	1·610	39·71
Suberic acid ..	171·79	138·7	0·6049	81·23	0 6831	1·439	39·42
Azalaic acid ..	191·45	153·1	0·6561	85·61	0·7013	1·221	38 00
Sabacic acid ..	210·41	167·5	0·6910	88·96	0·7148	1·109	37 69
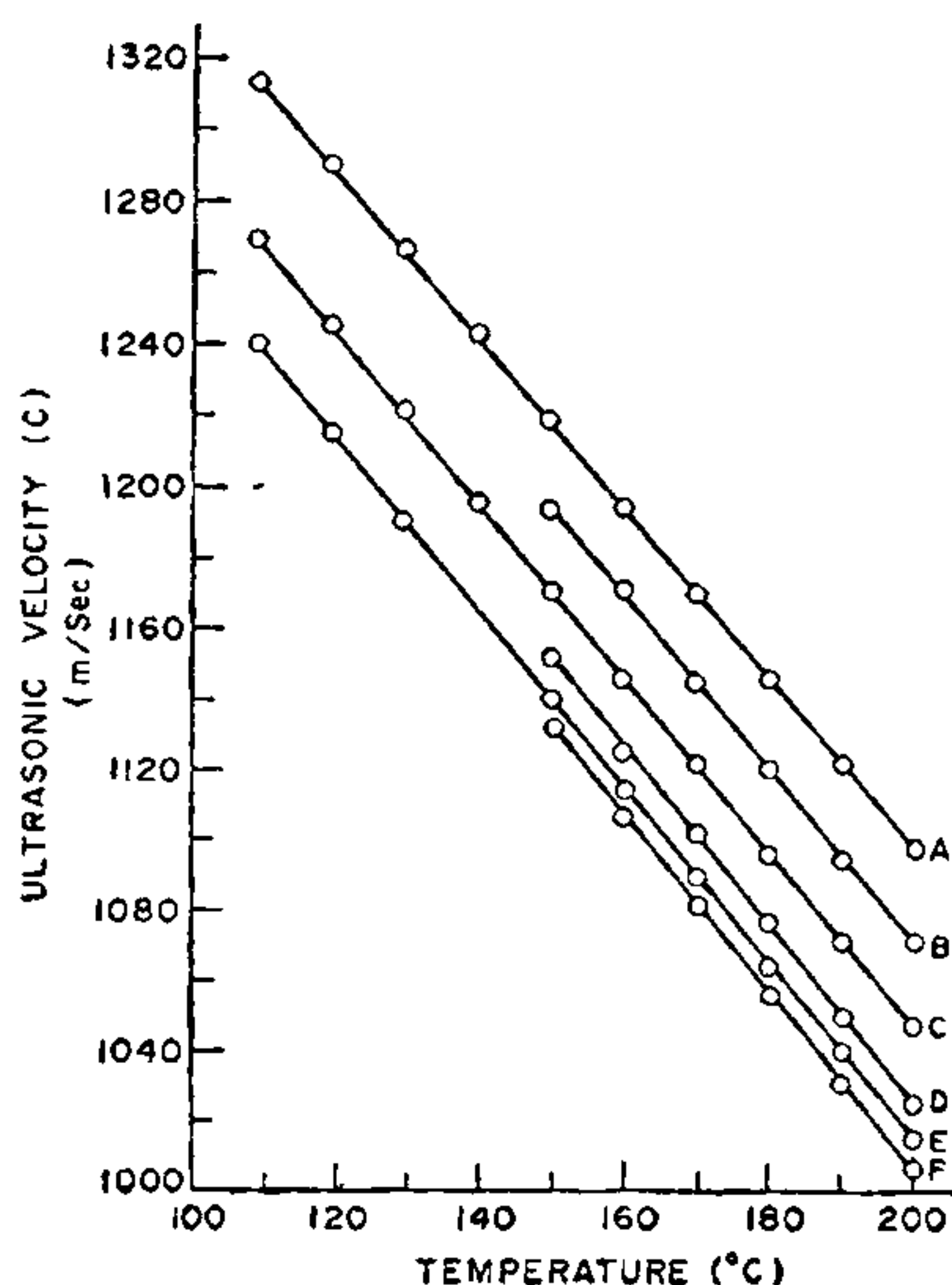
FIG. 1. Temperature variation of ultrasonic velocities. A, Glutaric acid; B, Adipic acid; C, Pimelic acid; D, Suberic acid; E, Azalaic acid; F, Sebacic acid.

extended the validity of Wada's relation to higher temperatures. He found that $(K/T^{\frac{1}{4}}) = 36$ with a maximum variation of $1·5\%$ upto a temperature of 157° C. Assuming the validity of Wada's linear relation between K and $\sqrt{T}$ in the present study, the value of K, corresponding to the temperature of 170° C, is found to be equal to 758.

According to general definition of free length

$$\text{L}_f = \frac{2 (V_T - V_0)}{[36\pi \text{ N } V_0^2]^{1/3}} \tag{2}$$

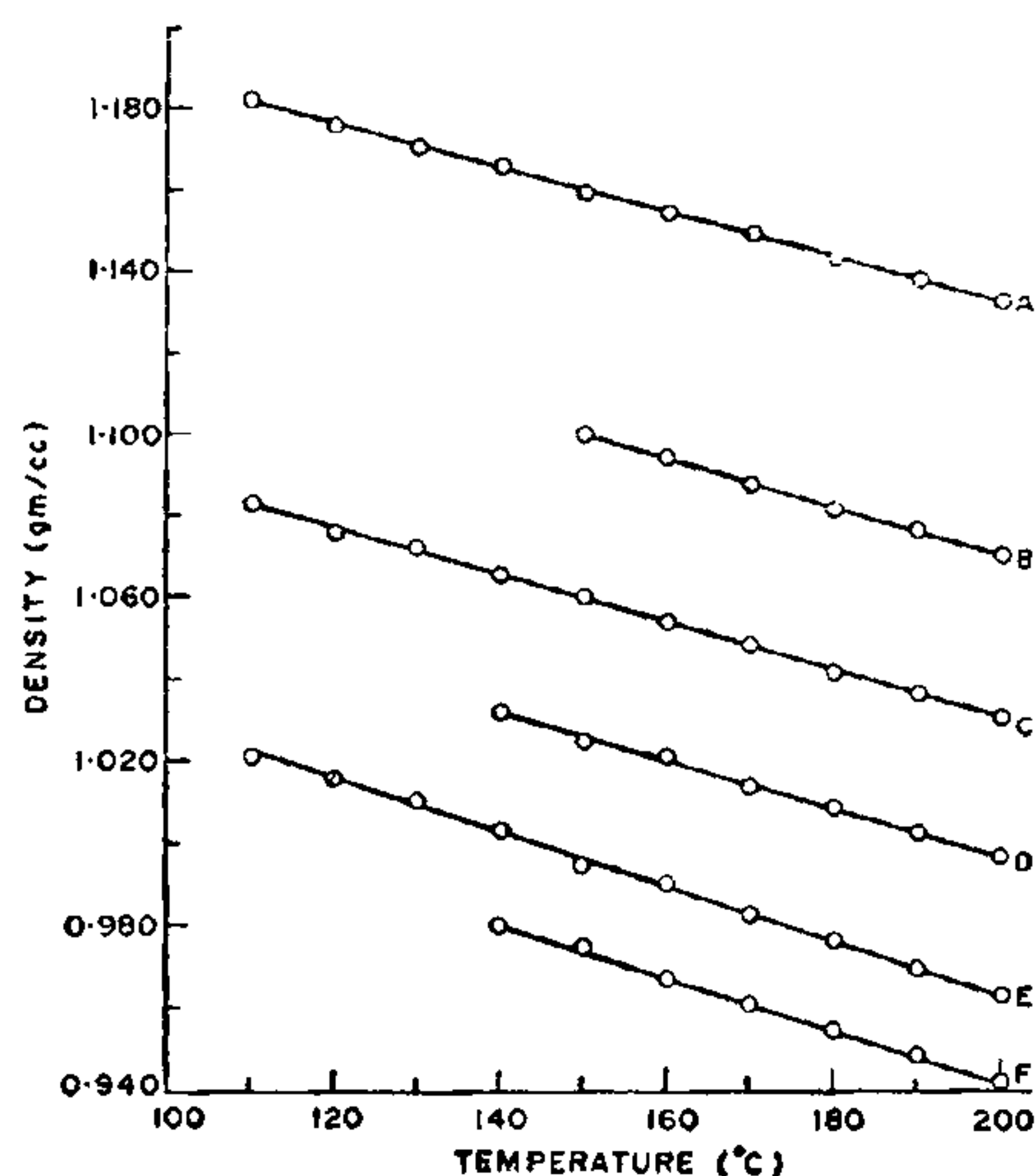where V_T is the volume at temperature T° K, V_0

FIG. 2. Temperature variation of densities of dicarboxylic acids.

is the volume at absolute zero and N is the Avogadro Number.

Volumes V_{170} at 170° C for each liquid is calculated by evaluating its density ρ_{170} from the density graphs shown in Fig. 2. V_0 is evaluated from Sugden's zero volume contributions. Values of V_{170}, and L_f for different liquids are shown in columns 2, 3 and 4 respectively of Table II.

The values of β_{ad} calculated for different liquids at 170° C and the values of L_f' calculated from equation (1) are shown in columns 5 and 6 respectively of Table II. A plot of L_f^2 against β_{ad} for different liquids with K = 758 is shown in
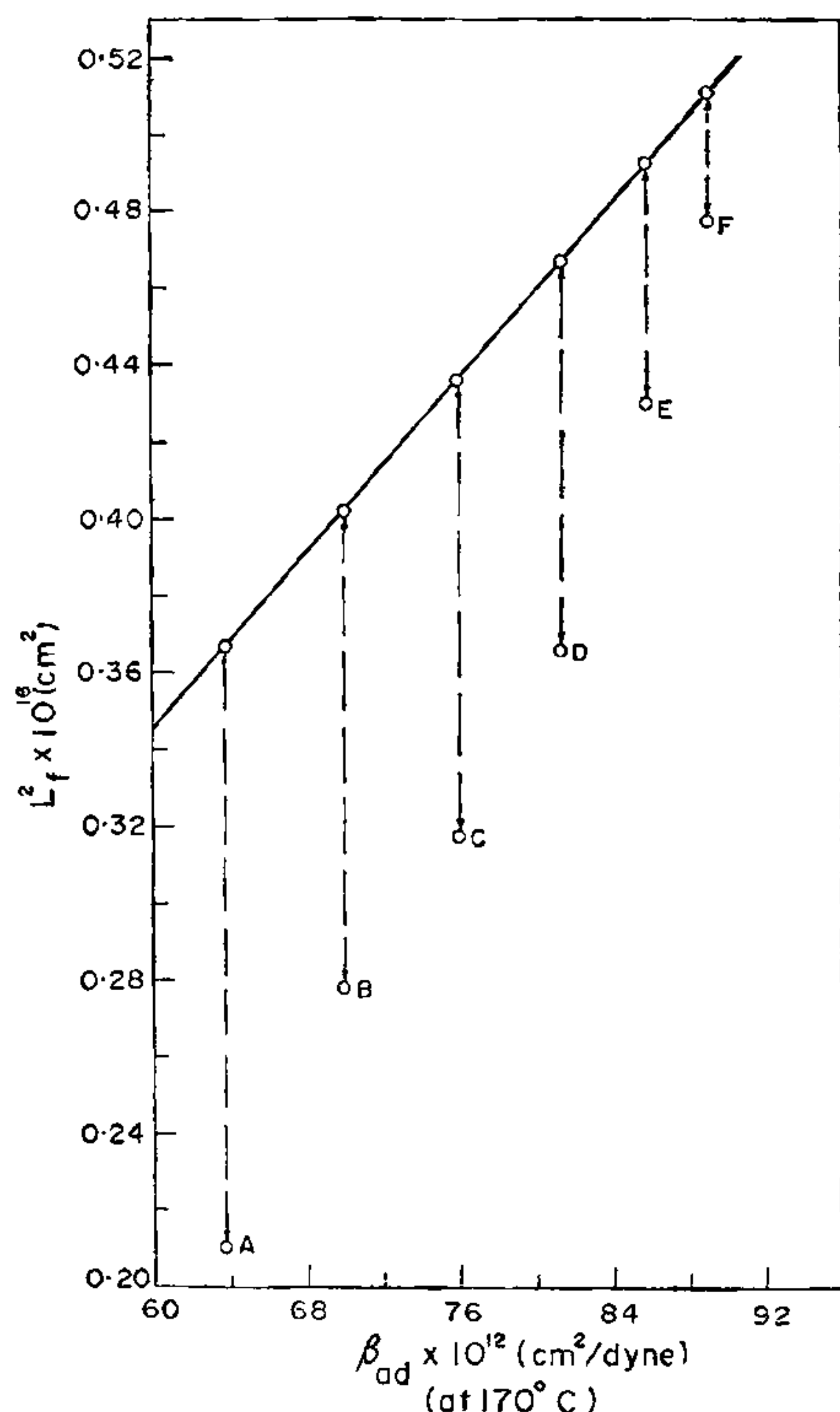
Fig. 3. Relationship between adiabatic compressibility and intermolecular free length of dicarboxylic acids at 170° C.

Fig. 3. All the evaluated points for different substances are found to lie below the straight line.

The association factors x calculated for different substances by the relation

$$z = \left[\frac{L_f'}{L_f}\right]^3$$

are shown in column 7 of Table II. It is interesting to observe that association decreases with increase of molecular weight of the acid. When association is taken into account, Lagemann's rule[9] for normal liquids is obeyed by these substances as well and the product $[xM]^{\frac{1}{3}} \triangle c/\triangle t$ is found to be constant as shown in column 8 of Table II with an average value of 39·08.

The first three members of the homologous series of dicarboxylic acids decompose near their melting points and as such their ultrasonic behaviour is being studied by solution method and their results will be published elsewhere.

ACKNOWLEDGEMENTS

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NUTRIENT COMPOSITION OF BARBADA OR MALMANDI (INDIGOFERA GLANDULOSA)

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ABSTRACT

The seeds of Indigofera glandulosa, a wild legume grown in some parts of Deccan region, have been analysed for nutrient composition and amino acid profile. The legume contains 26% protein and is a good source of minerals and B-complex vitamins. Aminogram and bioasay for acute toxicity reveal that the seeds do not contain undesirable constituents. The possibilities of exploiting such innocuous wild legumes with good nutritive potential for edible purposes have been discussed.

*I*NDIGOFERA GLANDULOSA, commonly known as barbada, malmandi or befri is an annual herb found in parts of U.P., Bihar, Gujarat and the Deccan plateau. It has been described as nutritious and is believed to possess the qualities of a tonic in Indian medicine[1,2]. Seeds of this wild legume are reported to contain 31% protein and cultivated varieties appear to contain even higher amounts[3] (37%). However, complete information on the nutrient composition and the