

3H), 3.95 (s, 3H), 3.53–3.80 (m, 4H) and 0.78 (d,  $J = 7.0$  Hz, 3H); MS at  $m/z$  444 ( $M^+$ , 74%), 426 (60), 408 (10), 390 (75), 265 (20), 146 (25), 133 (100) and 117 (80); Found: C, 62.0; H, 5.38; MeO, 13.85;  $C_{23}H_{24}O_9$  reqd., C, 62.16; H, 5.40;  $2 \times$  MeO, 13.96%; acetate ( $Ac_2O$ -Py), m.p. 205–7° (dec); pmr ( $CDCl_3$ , 90 MHz)  $\delta$ 8.0 (d,  $J = 8.5$  Hz, 2H), 7.0 (d,  $J = 8.5$  Hz, 2H), 6.70 (s, 1H), 6.39 (s, 1H), 4.90 (d,  $J = 7$ , OH, 1H), 4.0 (s, 3H), 3.90 (s, 3H), 3.55–3.80 (m, 4H), 2.10, 2.06, 2.04 and 1.70 (each s, 12H) and 0.78 (d,  $J = 7.0$  Hz, 3H); permethylether, m.p. 180–84°; ms at  $m/z$  500 ( $M^+$ , 76%), 485 (25), 307 (20), 188 (25), 175 (100) and 159 (80). 200 mg **2** was treated with phenol and HI as usual which yielded acacetin-5-methylether (m.m.p. and co-tlc). 100 mg **2** was oxidised with  $FeCl_3$  as usual to yield L-rhamnose (co-pc and rhamnosazone). cmr ( $CDCl_3$ ): aglycone,  $\delta$ 181.6, 164.3, 163.7, 161.1, 159.9, 156.9, 127.9 (2C), 120.9, 115.5 (2C), 108.5, 104.1, 102.8, 90.2, 56.0, 55.9; C-rhamnosyl,  $\delta$ 100.5, 72.2, 70.9, 70.43, 68.2 and 17.6.

**Compound-3:** M.p. 330–33°;  $\lambda_{max}^{MeOH}$  267, 335; +  $AlCl_3$  275, 340, 388; +  $AlCl_3 + HCl$  272, 305, 342, 389; +  $NaOAc$  286, 348; +  $NaOMe$  265, 402 nm;  $\nu_{max}^{KBr}$  3400, 2920, 2870, 1645, 1608, 1520, 1475, 1170, 1080, 1015, 895, 825 and 805  $cm^{-1}$ ; pmr ( $CDCl_3$ , 90 MHz)  $\delta$ 7.98 (d,  $J = 8.5$  Hz, 2H), 7.0 (d,  $J = 8.5$  Hz, 2H), 6.70 (s, 1H), 6.39 (s, 1H), 4.90 (d,  $J = 7.0$  Hz, 1H), 4.0 (s, 3H), 3.50–3.80 (m, 4H) and 0.78 (d,  $J = 7.0$  Hz, 3H), ms at  $m/z$  430 ( $M^+$ , 75%), 412 (60), 376 (75), 251 (20), 146 (25), 133 (100) and 117 (80); Found: C, 61.29; H, 5.10; MeO, 7.38;  $C_{22}H_{22}O_9$  reqd., C, 61.39; H, 5.12;  $1 \times$  MeO, 7.44%; acetate ( $Ac_2O$ -Py), m.p. 153–54°; pmr ( $CDCl_3$ , 90 MHz)  $\delta$ 8.0 (d,  $J = 8.5$  Hz, 2H), 7.0 (d,  $J = 8.5$  Hz, 2H), 6.70 (s, 1H), 6.39 (s, 1H), 4.90 (d,  $J = 7.0$  Hz, 1H), 4.0 (s, 3H), 3.50–3.80 (m, 4H), 2.10, 2.08, 2.03, 2.0 and 1.71 (each s, 15H) and 0.78 (d,  $J = 7.0$  Hz, 3H); permethylether, m.p. 198–99° (dec); ms at  $m/z$  500 ( $M^+$ , 75%), 485 (25), 307 (20), 188 (25), 175 (100) and 159 (80). 200 mg **3** was treated with phenol and HI as usual to afford genkwanin (m.m.p. and co-tlc). 100 mg **3** was reacted with  $FeCl_3$  by the earlier method to give L-rhamnose (co-pc and rhamnosazone). cmr ( $CDCl_3$ ): aglycone,  $\delta$ 181.5, 164.4, 163.7, 161.1, 159.9, 156.9, 127.9 (2C), 120.9, 115.6 (2C), 108.6, 104.1, 102.8, 90.2, 55.9; C-rhamnosyl,  $\delta$ 100.5, 72.2, 70.9, 70.43, 68.2 and 17.6.

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## EXCESS INTERNAL PRESSURE AND INTERMOLECULAR INTERACTION IN BINARY LIQUID MIXTURES

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INTERNAL pressure has been found to be a very important parameter<sup>1-7</sup> in sonochemical reactions<sup>8-15</sup> i.e. chemical reactions initiated or accelerated by ultrasonic waves). The increasing importance of internal pressure in the theory of liquid state<sup>16</sup> and in sonochemistry inspired us to investigate its

detailed behaviour in the case of homogeneous binary liquid mixtures. Thermodynamic and ultrasonic measurements provide a very important and accurate method for determination of internal pressure of liquids. Stavely *et al*<sup>17</sup> predicted interaction in liquid mixtures by comparing the internal pressure of individual liquid components. Dunlop and Scott<sup>18</sup> determined the internal pressure of perfluoron-*n*-hexane, *n*-hexane and their mixtures. They compared the values of internal pressure with the cohesive energy density for these mixtures. The study of intermolecular interaction in various binary liquid mixtures in the light of excess internal pressure is a subject of the present investigation.

The internal pressure  $P_i$  of liquid and liquid mixtures has been evaluated from the sound velocity  $C$  data using the following relation

$$P_i = \frac{\alpha T C_p M C^2}{\alpha^2 T V M C^2 + V C_p} - P, \quad (1)$$

which is obtained using the following familiar thermodynamic equations

$$(\partial E / \partial V)_T = T (\partial P / \partial T)_V - P = (\alpha T / \beta T) - P, \quad (2)$$

and

$$(\partial P / \partial T)_V = -(\partial V / \partial T)_P / (\partial V / \partial P)_T, \quad (3)$$

where

$$\alpha = 1/V (V/T)_P \text{ and } \beta_T = 1/V (\partial V / \partial P)_T.$$

In the above equations,  $\alpha$  is the thermal expansion coefficient,  $C_p$  stands for specific heat at constant pressure,  $M$  and  $V$  are molecular weight and molar volume of the liquid mixture respectively,  $\beta_T$  is the isothermal compressibility and  $T$  stands for temperature. The internal pressure for the ideal mixture is calculated from the following equation:

$$(P_i)_{id} = x_1(P_i)_{(1)} + x_2(P_i)_{(2)}. \quad (4)$$

Hence the excess internal pressure is given by

$$P_i^E = (P_i)_{mix} - (P_i)_{id}. \quad (5)$$

Here,  $x_1$ ,  $x_2$ ,  $P_{i(1)}$  and  $P_{i(2)}$  are the molefractions and internal pressure of components (1) and (2) respectively.

The internal pressure of the binary liquid mixtures of cyclohexane with isomeric xylene at 25, 40 and 50°C has been measured using thermodynamic data of Rajgopal and Subrahmanyam<sup>19</sup>. Table 1 shows that the internal pressure of all the mixtures presently studied decreases continuously with increase in temperature at all compositions like the

Table 1 Excess internal pressure of binary liquid mixtures

Temp.	$x_2$	$P_i^E$ (atm)
Cyclohexane + <i>o</i> -xylene		
25°C	0.2502	-17.6
	0.4978	204.5
	0.7497	451.2
40°C	0.2502	-262.8
	0.4978	-44.6
	0.7497	176.7
50°C	0.2502	-467.5
	0.4978	-264.5
	0.7497	-23.3
Cyclohexane + <i>m</i> -xylene		
25°C	0.2400	-35.0
	0.4989	157.0
	0.7505	443.3
40°C	0.2480	-211.9
	0.4989	-34.3
	0.7505	207.5
50°C	0.2480	-419.8
	0.4989	-253.0
	0.7505	-79.0
Cyclohexane + <i>p</i> -xylene		
25°C	0.2585	-31.8
	0.4973	165.7
	0.7463	344.4
40°C	0.2585	-235.6
	0.4973	-54.8
	0.7463	123.4
50°C	0.2585	-399.1
	0.4973	-250.0
	0.7463	-98.9

internal pressure of the individual organic liquids studied earlier<sup>17,20</sup>. Table 1 also shows that the excess internal pressure for systems cyclohexane + *o*-xylene at 25°C has negative value in the beginning which becomes positive at the mole fractions,  $x_2 = 0.4978$  and  $x_2 = 0.7497$ . At 40°C it has negative values at  $x_2 = 0.2502$  and  $x_2 = 0.4978$  which become positive at  $x_2 = 0.7497$ . But at 50°C it has negative values at all molefractions which vary with concentration. The same trend is observed in the case of cyclohexane + *m*-xylene and cyclohexane + *p*-xylene also, which clearly indicates intermolecular interaction in the mixture. The negative values at higher temperature indicate that intermolecular interaction increases with increase of temperature. The increasing magnitude of negative  $P_i^E$  values at higher concentration of cyclohexane indicates that interaction increases with increase of cyclohexane concentration at all temperatures.

It may therefore be concluded that the value of internal pressure of organic liquid mixtures decreases with increasing temperature as for pure organic liquids. The rate of fall varies from one system to another and may differ for different temperatures. Excess internal pressure is a powerful tool for predicting intermolecular interactions in homogeneous binary liquid mixtures. It varies with temperature and composition of the binary liquid mixtures. However, it is unable to accurately predict the type of interaction.

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### A LINK-CHANNEL OCCUPATIONAL SITE OF ACHEULIAN MAN, UPPER KRISHNA VALLEY, KARNATAKA

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UPPER Krishna valley has proved less fossiliferous and implementiferous in comparison to other peninsular river valleys. The earliest report of fossils from the valley is from the Gokak area<sup>1</sup>. It was after a lull of about a century, that a few more fossils were reported from Nittur<sup>2</sup>. Later discoveries from Bor-khal and Dhom dams<sup>3</sup> added to the faunal list in the subsequent years. However, no Acheulian sites have so far been reported from the Deccan Trap region of the Krishna valley, in association with fossil-fauna remains. The present communication reports the first finding of Acheulian artefacts from Yedurwadi, in association with vertebrate fossils.

The Acheulian tools were discovered in the link-channel of river Krishna near Yedurwadi (16° 35' 42"N and 74° 45' 42"E) in the course of a geomorphic investigation. The site is situated south of Shirguppi in the Belgaum district of Karnataka (figure 1).

The link-channel of Krishna has exposed older fluvial deposits. The stratigraphical column (figure 2) illustrates brown silts (sandy-silt) with calcretes at the base. These silts continue for about 5-7 metres below the present channel floor. From the upper part of this lithounit a fossilized tusk of *Elephas* sp was collected. Indurated sandy-pebbly gravel, rich in laterite pebbles unconformably rests over the basal brown silt. This indurated unit is also marked by lenses of fissured clays, 10-15 cm thick. Overlying this is a kankar-rich brown silty layer with occasional and dispersed pebbles. This fine member is overlain disconformably by about two metres of thick indurated sandy-pebbly-cobbly gravel. At the