

The Leucoanthocyanin could therefore be designated as Leucocyanidin 3-O- $\alpha$ -D-galactopyranoside.

The suggested structure was in conformity with its IR and NMR data.

IR:  $\nu_{\text{max}}^{\text{KBr}}$  ( $\text{cm}^{-1}$ ): 3320 (OH group), 1620, 1500, 1470 (aromatic ring), 1260, 1150, 1040 (w) and 822 (sugar moiety).

NMR: ( $\text{CDCl}_3$ , 60 MHz); (values in  $\tau$ ): 6.5 (m, 6-H, sugar protons), 5.80 (m, 1H, 3-H), 5.00 (m, 1H, 2-H), 4.70 (m, 1H, 4-H), 4.3 (m, H-1, galactosyl), 3.88 and 3.80 (each d, 2H, 6- and 8-H), ( $J_{6,8}$  2.3 C/S), 2.80 (d, 2H, 2'- and 6'-H).

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## EVALUATION OF EXCESS INTERNAL PRESSURE IN BINARY LIQUID MIXTURES OF WATER WITH ASSOCIATED LIQUIDS

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INTERNAL pressure has been used as an important parameter<sup>1-8</sup> to study the inter-molecular interactions between binary liquid mixtures. Pandey *et al.*<sup>9</sup> showed that excess internal pressure, like other thermodynamic properties varies with change in composition and temperature of the systems.

Recently excess internal pressure has been evaluated in binary liquid mixtures containing nonassociated liquids viz *n*-hexane + dichloromethane, *n*-hexane + 1,2-dichloroethane and *n*-heptane + dichloromethane, and *n*-heptane + 1,2-dichloroethane. The study has been extended to correlate this excess property with intermolecular interactions<sup>10</sup>. In the present investigation the associated organic liquid has been taken and the excess internal pressure has been evaluated in the binary liquid mixtures of water + *t*-butanol, water + *n*-propanol, water + ethylene glycol, and water + glycerol at 25°C. The ultrasonic velocity and density data have been taken from literature<sup>11</sup>.

### Theory:

The internal pressure was evaluated by the following equations:

$$P_i V \left(1 - \frac{d}{a}\right) = RT, \quad (1)$$

$$v = a^3 / \sqrt{2}, \quad (2)$$

$$P_i = \frac{2^{1/6} RT}{(2^{1/6} V - d N^{1/3} V^{2/3})}, \quad (3)$$

$$d^{5/2} = \frac{1}{7.21 \times 10^{19}} \cdot \frac{V r^{1/4}}{T_c^{1/4}}, \quad (4)$$

$$T_{c_m} = \sum_{i=1}^2 X_i T_{c_i}, \quad (5)$$

$$r = 6.30 \times \rho \times U^{3/2} \times 10^{-4}. \quad (6)$$

All the symbols in (1) to (6) have the usual significance described elsewhere<sup>10</sup>.

The excess internal pressure is given by

$$P_i^E = P_{i(m)} - \sum_{i=1}^2 X_i (P_i)_{id}. \quad (7)$$

The rigid sphere diameter obtained from (4) and the excess internal pressure obtained from (7) are listed in table 1. The excess internal pressure versus the mole-fraction of the first component has been plotted for the different systems. The excess internal pressure ( $P^E$ ) has been fitted by the method of least squares to the equation

$$P^E = x_1(1-x_1) \sum_{i=0}^2 C_i(2x_1-1)^i, \quad (8)$$

where  $x_1$  is the molefraction of water and  $C_i$ 's are constants characteristic of a system. The values of the

**Table 1** Values of rigid sphere diameter  $d$  and excess internal pressure  $P^E$  for different systems at 25°C.

$x_1^*$	$d$ A	$P^E$ Kbar
<b>Water + <i>t</i>-butanol</b>		
1.0000	2.7190	—
0.9143	3.0463	-0.757
0.8686	3.1805	-1.168
0.7405	3.5314	-1.648
0.5413	3.9852	-1.614
0.3556	4.3792	-1.154
0.2174	4.6343	-0.733
0.0000	5.0024	—
<b>Water + <i>n</i>-propanol</b>		
1.0000	2.7190	—
0.9149	2.9747	-0.529
0.8833	3.0518	-0.741
0.7314	3.3905	-1.300
0.5740	3.7046	-1.329
0.3651	4.0764	-1.285
0.2146	4.3189	-0.627
0.0000	4.6441	—
<b>Water + ethylene glycol</b>		
1.0000	2.7190	—
0.9540	2.8397	-0.090
0.9030	2.9638	-0.169
0.6870	3.4027	-0.409
0.5390	3.6523	-0.465
0.3673	3.9097	-0.417
0.2521	4.0679	-0.323
0.0000	4.3838	—
<b>Water + glycerol</b>		
1.0000	2.7190	—
0.9889	2.7703	-0.110
0.9287	2.9892	-0.272
0.8589	3.2203	-0.389
0.7044	3.6550	-0.578
0.5441	4.0335	-0.621
0.2356	4.6186	-0.347
0.0000	4.9927	—

$x_1^*$  represents the mole fraction of water.

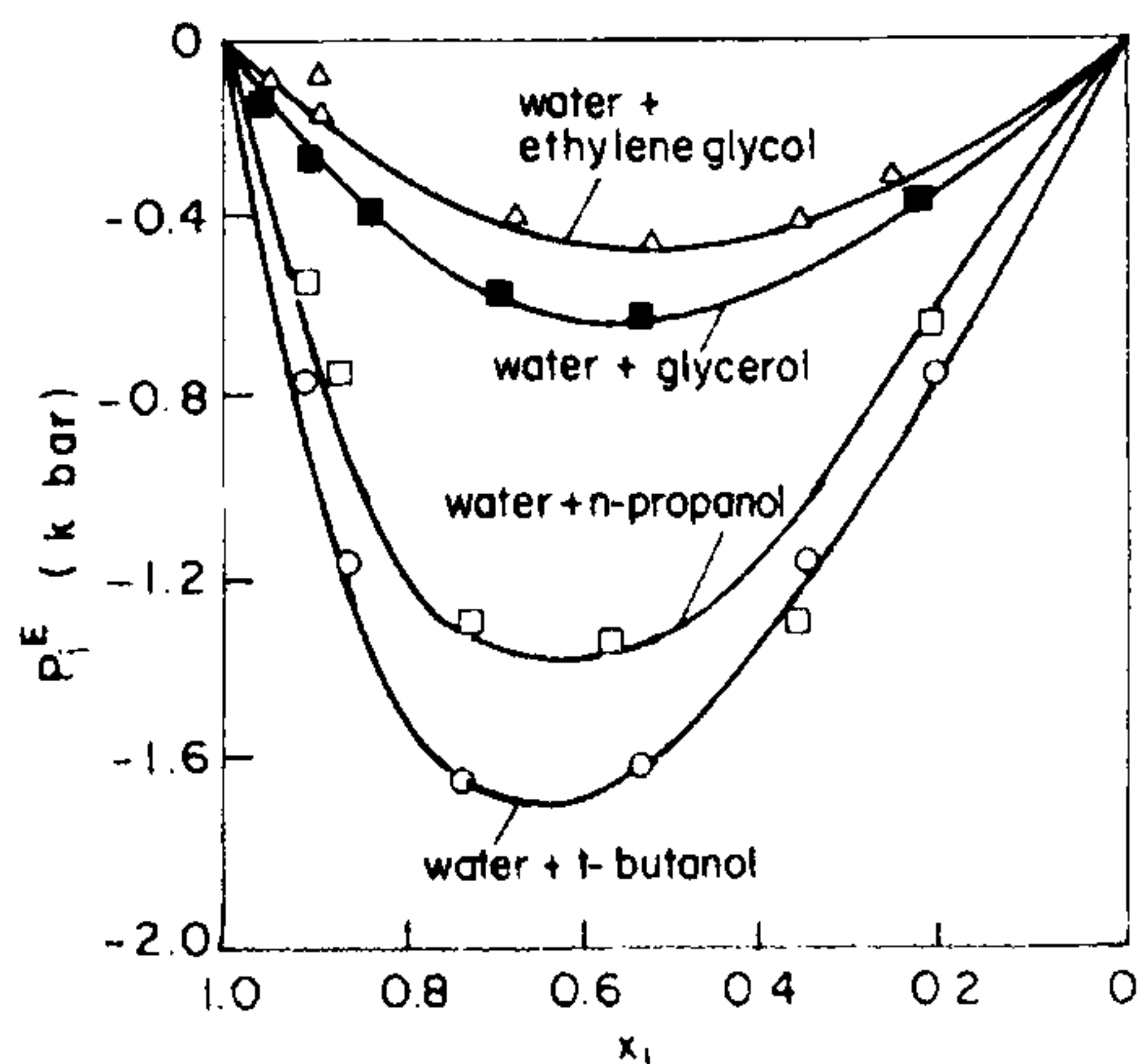
constants  $C_i$ 's of (8) are given in table 2 which also includes the values of the standard deviations,  $\sigma(P^E)$ , which have been calculated from the relation

$$\sigma(P^E) = [(\Delta P^E)^2 \times (m-n)^{-1}]^{1/2}, \quad (9)$$

where  $m$  is the number of observations and  $n$  is the number of constants used in (8). A perusal of table 1 and figure 1 indicates that  $P^E = P^E(x)$ . It is also evident from figure 1 and table 1 that intermolecular interaction in the case of water + monohydric alcohols is stronger than that of water + polyhydric alcohols. When monohydric alcohols are mixed with water, hydrogen bonding between like molecules is broken down and hydrogen bonds are formed between unlike molecules. In the case of polyhydric alcohols mutual

**Table 2** Values of the constant  $C_i$ 's of equation (8) and standard deviation  $\sigma(P^E)$  at 25°C.

	$C_0$ Kbar	$C_1$ Kbar	$C_2$ Kbar	$\sigma(P^E)$
Water + <i>t</i> -butanol	-6.1324	-3.783	-1.4507	0.02
Water + <i>n</i> -propanol	-5.6322	-2.3732	+0.9092	0.04
Water + ethylene-glycol	-2.1112	-0.7249	+0.7008	0.03
Water + glycerol	-2.4012	-0.8544	+0.8124	0.04



**Figure 1.** Plot of  $P^E$  vs mole fraction ( $x_1$ ) of the first component.



association between their molecules is stronger than with water molecules so that strength of interaction decreases in these systems. This contention receives support from the Gruneisen parameter and excess internal pressure values for the same systems evaluated by Murthy *et al*<sup>1,2</sup> using thermal pressure coefficient and isothermal compressibility data.

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## OCCURRENCE OF SKARN ROCKS IN THE CHAUR AREA, HIMACHAL HIMALAYA, INDIA.

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THE Jutogh metamorphites, exposed in the Himachal Himalaya, form a large thrust sheet resting over the Chails in the Simla Hills and Chaur Mountain. In the Chaur area, south-east of Simla, the Jutogh consists of

metasediments with occasional bands of marble/crystalline limestone and are associated with gneisses and granite which are traversed by metabasic sills and dykes. The granite occupies the top of the Chaur Peak. The metasediments together with the carbonate rocks belong to greenschist and amphibolite facies and show Barrovian type of metamorphism reaching upto sillimanite-muscovite zone of Turner<sup>1</sup>.

The carbonate rock in the high-grade zone is metasomatically transformed into skarn rocks which outcrop along Sarpat nala and at other places in sillimanite-bearing pelitic schist intimately associated with gneisses. It is about 20–60 feet in thickness and often intensely folded. The typical skarn is heavy, medium-grained, dark green to pinkish in colour. The green and pink colours are mainly on account of clinopyroxene and garnet together with a little amphibole with or without sphene and epidote. This rock has been misidentified as eclogite by Srikantia *et al*<sup>2</sup> and later redesignated as calc-silicate by Bhargava and Chopra<sup>3</sup> on the basis of grossularite instead of pyrope garnet. A detailed petrographic and chemical study of these rocks, especially electron microprobe data, revealed that the rock reported as eclogite consists of hedenbergite ( $\text{Ca}_{0.446-0.510} \text{Fe}_{0.433-0.442} \text{Mg}_{0.035-0.136} \text{Mn}_{0.003-0.008} \text{Si}_{0.964-1.015} \text{O}_3$ ), ferrohastingsite (100 Mg: Mg + Fe<sup>\*2+</sup> + Mn 5.77–13.88) and grossular (48.64–65.02 mol. %)–almandine (32.65–49.84 mol. %) garnet and subordinate calcite with or without sphene, epidote, quartz, microcline, plagioclase, etc. Some such rocks essentially consist of clinopyroxene, grossular-almandine garnet with little calcite and amphibole, are surrounded by banded rocks; the dark bands being rich in amphibole and scarce in clinopyroxene while the light bands consist of epidote, quartz, calcite, sphene, scapolite, k-feldspar, plagioclase and sometimes garnet. This rock is highly variable in mineral constituents in volume percentage. Such rocks are dominant in amphibole and contain garnet while others are scarce in amphibole and rich in epidote, clinozoisite, quartz, sphene and calcite. Srikantia *et al*<sup>2</sup> seem to have designated some of these rocks as pyroxenite and garnetiferous amphibolite.

Despite a considerable iron enrichment in the skarn, relative to the original carbonate, iron oxides are absent from the skarn of the Chaur area. Garnet and clinopyroxene are replaced by symplectic intergrowth of iron-rich amphibole, calcite and quartz and the amphibole shows replacive relation with calcite. It also replaces epidote and scapolite replaces plagioclase. In a

\* Total iron as Fe<sup>2+</sup>