

## EVALUATION OF EXCESS INTERNAL PRESSURE AND CORRELATION WITH INTERACTION IN BINARY LIQUID MIXTURES

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### ABSTRACT

Excess internal pressure has been evaluated in binary liquid mixtures of *n*-hexane + dichloromethane, *n*-hexane + 1,2-dichloroethane and *n*-heptane + dichloromethane, *n*-heptane + 1,2-dichloroethane and an attempt made to correlate it with intermolecular interaction. It has been found that it provides a successful means for the interaction studies in binary liquid mixtures.

### INTRODUCTION

INTERNAL pressure, which is the result of the forces of attraction and repulsion between molecules in a liquid, is a very important parameter in the theory of liquid state. Extensive attempts have been made to show the significance of internal pressure as a fundamental property of liquid state and its correlation with other properties<sup>1-10</sup>. Stavely *et al*<sup>11</sup> compared the internal pressure of individual liquid components and predicted the interaction in liquid mixtures. Collins *et al*<sup>12</sup> used thermodynamic and ultrasonic measurements to determine the internal pressure of liquids. Pandey *et al*<sup>13</sup> extended the studies to binary liquid mixtures and showed that excess internal pressure, like other thermodynamic properties, varies with change in composition and temperature in the systems. In the present investigation a new attempt has been made to evaluate the excess internal pressure in binary liquid mixture and the study has been extended to correlate this excess property with intermolecular interactions.

### THEORETICAL

Buchler *et al*<sup>14,15</sup> obtained the following relation for internal pressure

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

where  $P_i$ ,  $V$ ,  $d$ ,  $a$ ,  $R$  and  $T$  represent internal pressure, molar volume, molecular diameter, shortest distance between the nearest neighbours, gas constant and absolute temperature respectively. The volume  $v$  per mole ( $v = V/N$ , where  $N$  is the Avagadro's number) is related to the distance between the nearest neighbours by the relation,

$$v = a^3 \sqrt{V^2}. \quad (2)$$

Using (1) and (2) and with suitable adjustment, one

gets

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

where  $d$  is the rigid sphere diameter of the molecule which can be obtained from the following relation<sup>16</sup>

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

$T_{c(m)}$ , the critical temperature of the mixture using the following simple relation<sup>17</sup>

$$T_{c(m)} = \sum_{i=1}^2 X_i T_{c_i}. \quad (5)$$

The excess internal pressure is defined as the difference between the internal pressure of the mixture  $P_{i(m)}$  and that of an ideal mixture of the same composition which is given by the relation

$$P_i^E = P_{i(m)} - \sum_{i=1}^2 X_i (P_i)_{id}. \quad (6)$$

### RESULTS AND DISCUSSION

The rigid sphere diameter  $d$  obtained from (4) and the excess internal pressure obtained from (6) are listed in table 1. The necessary data for the calculation of  $P_i^E$  have been taken from the literature<sup>18</sup>. The excess internal pressure ( $P_i^E$ ) has been fitted by the method of least squares to the equation.

$$P_i^E = x_1 x_2 [A + B(x_1 - x_2) + C(x_1 - x_2)^2], \quad (7)$$

where  $A$ ,  $B$  and  $C$  are the constants which are characteristic of a system and  $x_1$  and  $x_2$  are mole fractions of components 1 and 2 respectively. The values of the constants  $A$ ,  $B$  and  $C$  are given in table 2.

The excess internal pressure has been plotted versus the mole fraction of the first component for the

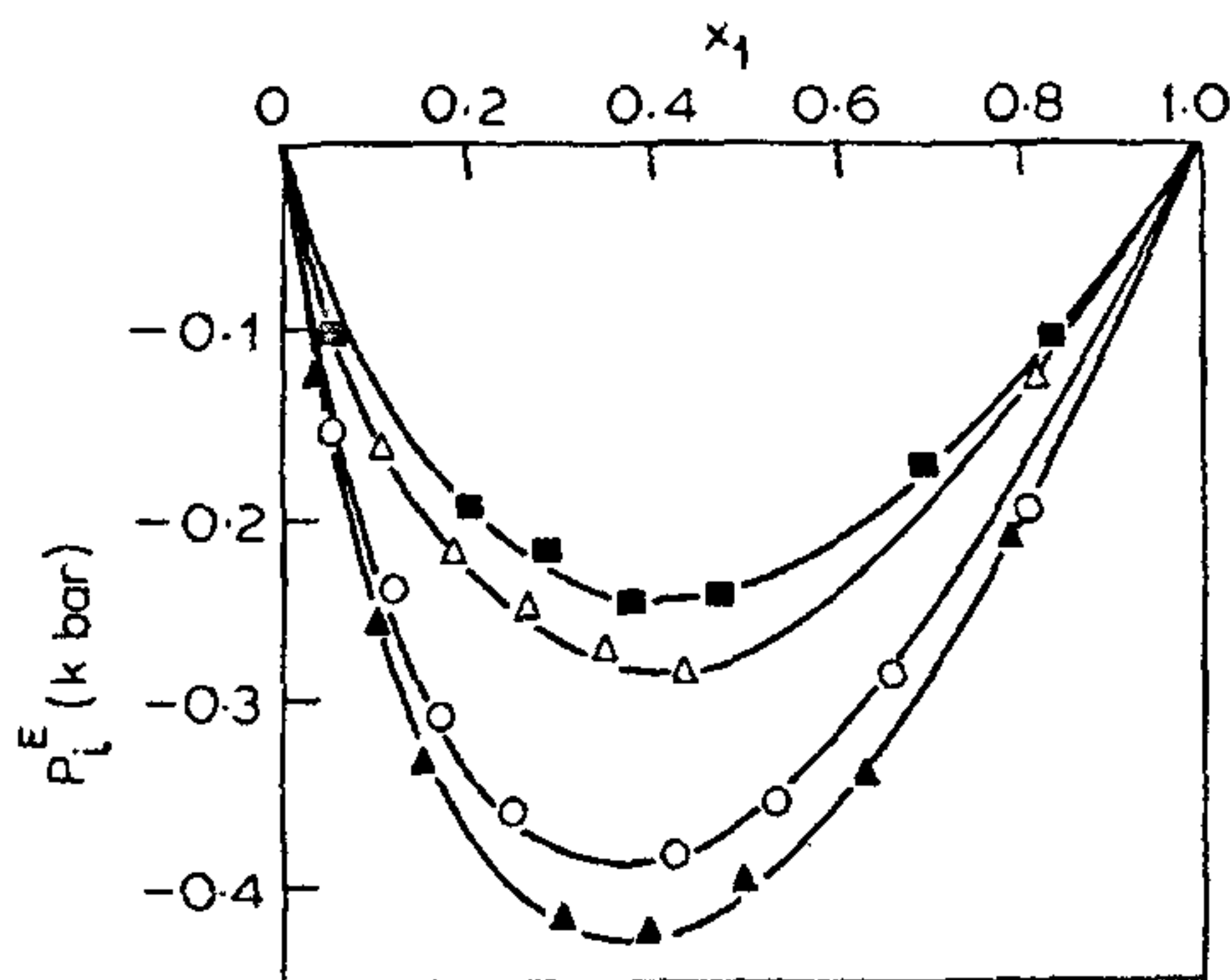
**Table 1** Values of rigid sphere diameter  $d$  and excess internal pressure  $P_i^E$  for different systems at 30°C.

$x_1^*$	$d$ Å	$\frac{P_i^E}{\text{kbar}}$
<b>n-Hexane + dichloromethane</b>		
0.0000	4.5388	—
0.0531	4.6089	-0.154
0.1119	4.6827	-0.242
0.1117	4.7630	-0.310
0.2518	4.8547	-0.363
0.3353	4.9574	-0.392
0.4308	5.0644	-0.381
0.5408	5.1922	-0.362
0.6689	5.3008	-0.295
0.8197	5.5017	-0.199
1.0000	5.6192	—
<b>n-Hexane + 1,2 dichloroethane</b>		
0.0000	4.9324	—
0.2057	5.0698	-0.191
0.2871	5.1280	-0.228
0.3767	5.1940	-0.247
0.4754	5.2652	-0.244
0.7073	5.4240	-0.177
0.8448	5.5148	-0.100
1.0000	5.6192	—
<b>n-Heptane + dichloromethane</b>		
0.0000	4.5388	—
0.0464	4.6173	-0.123
0.0986	4.7137	-0.251
0.1579	4.8190	-0.331
0.3044	5.0686	-0.427
0.3963	5.2065	-0.438
0.5054	5.3584	-0.407
0.6367	5.5387	-0.344
0.7979	5.7200	-0.210
1.0000	5.9225	—
<b>n-Heptane + 1,2 dichloroethane</b>		
0.0000	4.9324	—
0.0564	4.9898	-0.100
0.1186	5.0532	-0.168
0.1876	5.1235	-0.222
0.2642	5.2042	-0.256
0.3503	5.2958	-0.276
0.4469	5.3957	-0.281
0.8292	5.7621	-0.120
1.0000	5.9225	—

$x_1^*$  mole fraction of the first component

different systems in figure 1. A perusal of table 1 and figure 1 indicates that  $P_i^E = P_i^E(x)$ . Figure 1 also indicates that the values of  $P_i^E$  for the system *n*-hexane + dichloromethane are greater in magnitude than the corresponding values for the system *n*-hexane + 1,2 dichloroethane. This variation in the values of  $P_i^E$  for these two systems may be due to difference in the nature of dichloromethane and 1,2 dichloroethane molecules. Dichloromethane is a polar molecule (1.6D) while 1,2 dichloroethane exists in both trans and gauche form. It is also interesting to note that the values of excess internal pressure for the systems *n*-heptane + dichloromethane and *n*-heptane + 1,2 dichloroethane are greater in magnitude than the corresponding values for the systems *n*-hexane + dichloromethane and *n*-hexane + 1,2-dichloroethane.

This is perhaps due to the greater size of  $\begin{array}{c} | \\ -C-C- \\ | \end{array}$  chain in *n*-heptane molecule in which the possibility of random coiling due to internal rotation about the  $\begin{array}{c} | \\ -C-C- \\ | \end{array}$  bond is more. Since a negative excess function



**Figure 1.** Plot of  $P_i^E$  vs mole fraction ( $x_1$ ) of the first component. (○) *n*-hexane + dichloromethane, (■) *n*-hexane + 1,2-dichloroethane, (▲) *n*-heptane + dichloromethane (Δ) *n*-heptane + 1,2-dichloroethane.

**Table 2** Values of constants  $A$ ,  $B$  and  $C$  of equation (7) and the standard deviation  $\sigma$  at 30°C.

	$A/\text{kbar}$	$B/\text{kbar}$	$C/\text{kbar}$	$\sigma$
<i>n</i> -Hexane + dichloromethane	-1.4053	+0.6673	-1.068	0.01
<i>n</i> -Hexane + 1,2-dichloroethane	-1.051	+0.333	+0.3918	0.02
<i>n</i> -Heptane + dichloromethane	-1.642	+0.331	-1.199	0.02
<i>n</i> -Heptane + 1,2-dichloroethane	-1.015	+0.515	-0.424	0.01

is an indication of strong interaction it may be concluded that intermolecular interaction in *n*-heptane molecule is greater than *n*-hexane molecule.

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## SOME ASPECTS OF PERALKALINE RHYOLITE GENESIS

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### INTRODUCTION

**P**ERALKALINE rhyolites are generally geochemically more fractionated than metaluminous rhyolites and associated with transitional or mildly alkaline alkali basalts. A model is presented in an attempt to explain the above observation. Before continuing, however, it should be stated that peraluminous rhyolites are to be excluded from the following discussion. Crustal contamination of magmas in the below fractional crystallisation model, based upon feldspars, will be assumed to be minimal. The terms "peralkaline", "metaluminous" and "peraluminous" are based upon the Shand classification which utilizes silica and alumina saturation<sup>1</sup>.

### THE ROLE OF FELDSPARS IN FRACTIONATION

The feldspar mineralogies of the basalt-peralkaline rhyolite and basalt-metaluminous rhyolite series are

important in the crystal fractionation histories of the two series. In southeast Queensland, Australia, it appears that for the tertiary peralkaline rhyolite series, as the parental mafic melt differentiates, the crystallising plagioclase becomes increasingly more albitic at first and thereafter becomes an anorthoclase. In effect, we have at any one stage in the crystal fractionation history of the series the one feldspar, initially a plagioclase and finally, after a "continuum" of compositional modification, an anorthoclase. The intermediate rocks are characterised by one feldspar-bearing (anorthoclase) trachytes. Data on bulk rock and feldspar compositions for this series are plotted<sup>2,3</sup> in figures 1 and 2 and shown in table 1.

On the other hand, the tertiary metaluminous rhyolite series in southeast Queensland, in a crystal fractionation model, is characterised by the crystallisation of plagioclase in the differentiating parental mafic melts and thereafter, in the derived and differentiating trachytes, by the crystallisation of co-existing plagioclase and sanidine. In the metaluminous