VOLUME CHANGE OF MIXING

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ABSTRACT

Excess volume of benzene-carbon Atetrachloride and benzene-1, 2-dichloroethane have been measured as functions of temperature and composition by a dilatometric method. Excess volumes predicted by cell model and average potential model are compared with experimental values available in the literature.

Key words: Volume-mixing-benzene-carbon tetrachloride-1, 2-dichloroethane-dilatometer-theory-solution.

1. INTRODUCTION

Volume change of mixing or excess volume per mole of a binary mixture is given by:

$$V^M = V - x_1 V_1^0 - x_2 V_2^0 \qquad (1)$$

Here, the mixture as well as the corresponding pure components are considered at the same temperature and pressure. Usually, the ordinary external pressure of one atmosphere is taken as the reference pressure.

Experimental determination of volume change of mixing is useful in verifying the validity of the theory of solutions and in determining which theory conforms most to the actual facts. Excess thermodynamic functions like excess volume, excess free energy, etc., represent the deviations from the laws of perfect solution.

In this work, volume change of mixing of benzene-1, 2-dichloroethane and benzene-carbon tetrachloride is determined over a range of temperature of 30–50° C by using a weight dilatometer.

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2. EXPERIMENTAL ARRANGEMENT

The weight dilatometer used in the present work is shown in Fig. 1. The volume is 5 cm^3, approximately 3 cm^3 being allowed for solutions and 2 cm^3 for mercury. The main body of the dilatometer is blown from 14 mm I.D. Corning glass tubing and this is fused to a 1 mm capillary side

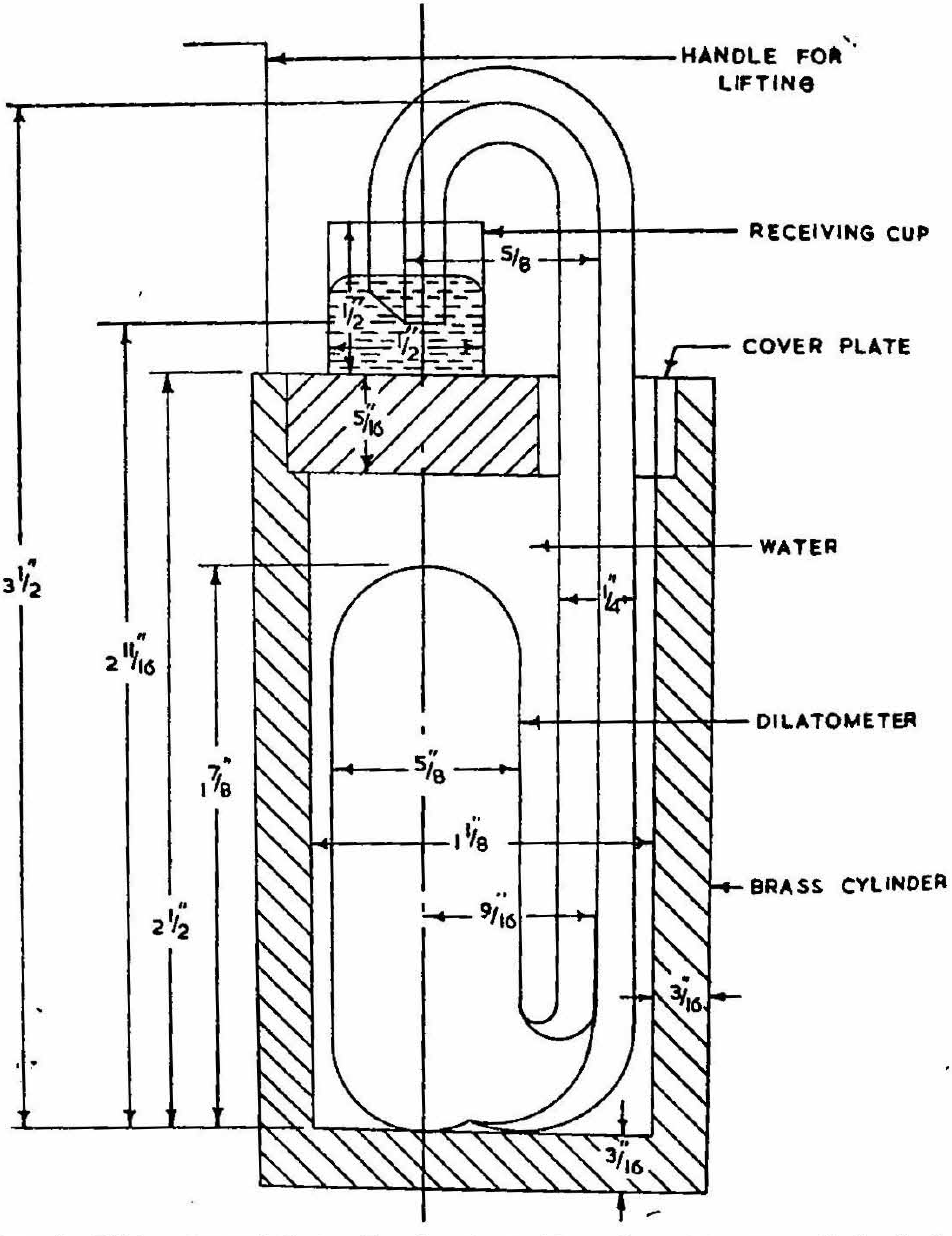


FIG. 1. Dilatometer and Casing Showing the Position of Receiving Cup. Scale : 2 : 1

tube. The tip of the capillary is tapered and ground at an angle of 45°, as suggested by Wood and Brusie [1], to avoid any air bubble clinging to the tip when the dilatometer is filled. The brass casing and cover plate are made from a 1½" diameter brass rod. A region of constant temperature is provided to the dilatometer by a thermostat with an on-off controller, which maintains temperature to ± 0·03° C. Figure 2 shows the arrange-

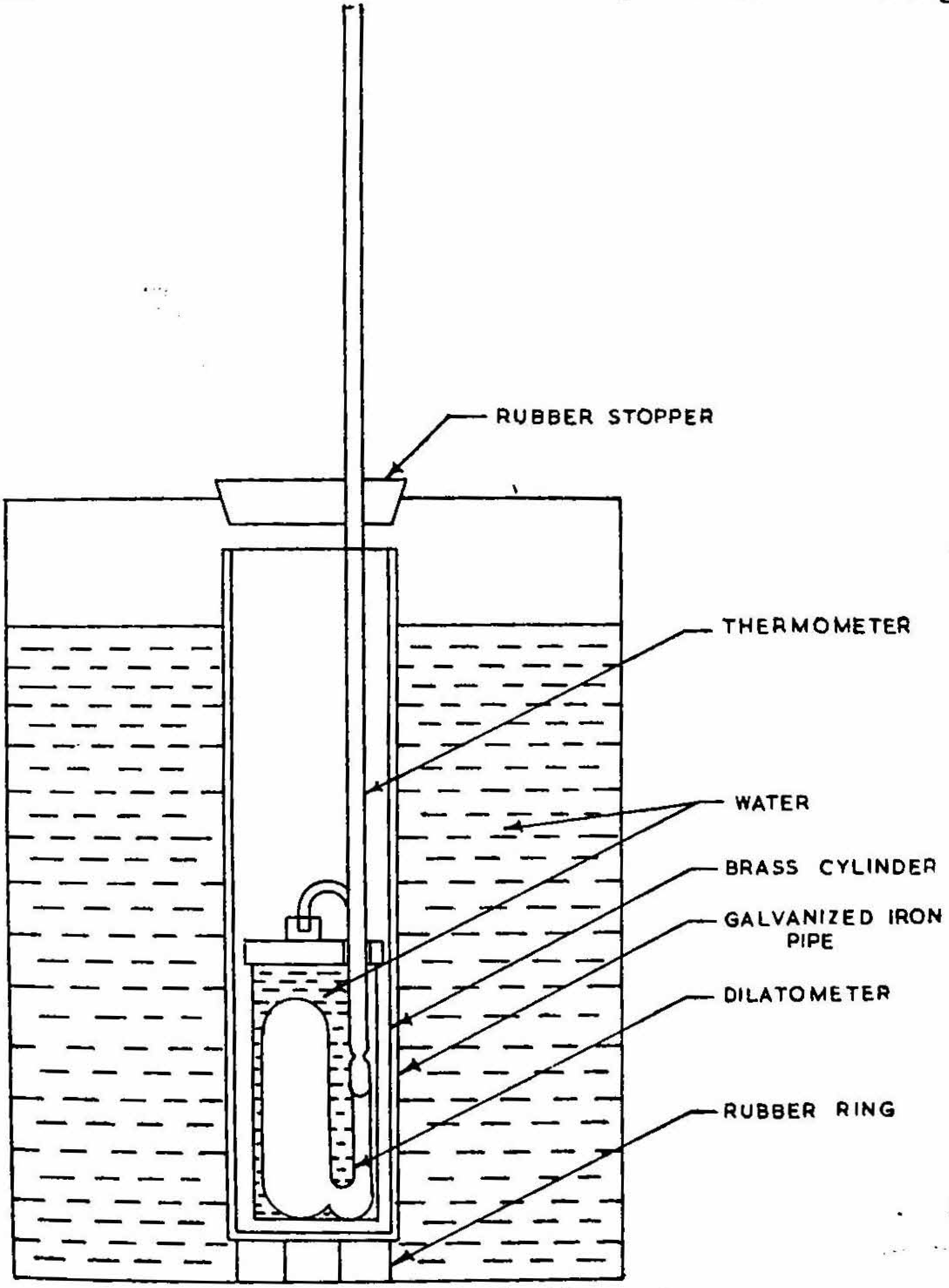


FIG. 2. Set-up in the Thermostat.

ment of the dilatometer in the thermostat. The filling of dilatometer is done in a similar manner described by Burlew [2].

3. DETERMINATION OF VOLUME CHANGE ON MIXING

The dilatometer is first cleaned with concentrated nitric acid to remove traces of mercury. It is then washed with water, dried by repeated heating and cooling. The dilatometer is first weighed empty and then after filling to about 1/3 the total volume with mercury and finally after filling the remaining portion with the liquid mixture. From these, the weight of the liquid taken in the dilatometer is calculated. After the capillary is dried, the dilatometer is placed in the brass cylinder with receiving cup in position. The mercury thread in the capillary is then joined with mercury in the receiving cup by gently heating the brass cylinder. Each series of experiments is started at 30° C. Then, the apparatus is kept in the thermostat. After the water inside the holder attains the temperature of the bath, the set up is left undisturbed for 15 minutes to allow the contents to attain steady state temperature. After this, the end of the capillary tube is separated from the receiving cup and then the brass cylinder with dilatometer and receiving cup is removed from the thermostat. The dilatometer is now removed from the cylinder and dried. The receiving cup and the dilatometer are now weighed separately. The dilatometer is again kept in the brass cylinder and the mercury thread in the capillary is joined with mercury in the receiving cup. The experiment is repeated at the next higher temperature. To correct for mercury evaporated from the collecting cups during the course of a run, the following procedure is adopted. A second cup of approximately the same size is always placed beside the collecting cup in order to determine this loss. The reduction in total weight of dilatometer *plus* receiving cup gives the total loss of mercury during a run. The reduction in weight of the dummy receiving cup for the same period gives the loss of mercury from the receiving cup and hence loss of mercury from the dilatometer can be calculated. This weight is added to the weight of mercury in the dilatometer to give the correct weight of mercury in dilatometer at each temperature. Knowing the weights of mercury in dilatometer and densities of mercury at various temperatures, volume of mercury in the dilatometer can be calculated. By knowing the total volume of dilatometer at various temperatures, the volume of liquid and hence the density at various temperatures can be evaluated.

First the dilatometer is calibrated by determining volume at 30° C, 35° C, 40° C, 45° C and 50° C by a series of measurements using water and mercury.

The densities of water and mercury at various temperatures used in this work is given in Table I. The density bottle is calibrated by measuring the weight of distilled water that fills the bottle. The calibrated density bottle is used in the determination of density-composition relationship.

TABLE I

Densities of water and mercury [4]

Temperature °C	Density of Mercury gm/cm³	Density of Water gm/cm³
30	13·5213	0·99568
35	13·5091	0·99406
40	13·4969	0·99225
45	13·4847	0·99025
50	13·4725	0·98070

Since the composition of the solutions used in the dilatometer cannot be determined directly, it is necessary to determine the density composition curve at one temperature. The densities of pure components and binary mixtures with mole fractions ranging from 0·1 to 0·9 in steps of 0·1 are determined using the calibrated density bottle. Knowing compositions and densities of liquid mixtures, the volume change on mixing is evaluated using the equations:

$$V^M = V - V^0 \tag{5}$$

where,

$$V = \frac{M_1x_1 + M_2x_2}{d} \tag{6}$$

$$V^0 = \frac{M_1x_1}{d_1} + \frac{M_2x_2}{d_2}\,. \tag{7}$$

With $V =$ molar volume of the mixture; $d =$ density of the mixture; $x_i =$ mole fraction of component i and $M_i =$ molecular weight of component i.

4. PURIFICATION OF LIQUIDS

Two litres of distilled water is redistilled in a flask and the middle 1/3 portion is collected. To this, about 0·2 gm of potassium permanganate and 0·5 gm of sodium hydroxide are added and again distilled. About 250 cm^3 of the middle fraction is collected and used in this work.

Mercury is first washed with distilled water. It is covered with a layer of 10 per cent nitric acid and air is bubbled through it. The acid is separated by filtration and mercury is washed repeatedly by distilled water to remove traces of acid. Mercury is then dried and used in the experiments.

All the organic liquids are purified by distilling twice in a packed distillation column. The purity is checked by density measurements. Density data is given in Table II.

TABLE II

Densities of organic liquids at 30° C

Liquid	This work gm/cm^3	Literature values	Reference
Carbon tetrachloride ..	1·5748	1·57503 1·57460	1 3
Benzene ..	0·8678	0·86810 0·86845	3 1
1, 2-dichloroethane ..	1·2383	1·23815 at 30·1°C	3

5. RESULTS AND DISCUSSION

The density values are fitted by the method of least squares to a third degree polynomial in composition. The curves obtained are:

For benzene-carbon tetrachloride system:

$$d = 1{\cdot}57471 - 0{\cdot}65344 \times 10^{-2} x - 0{\cdot}46915 \times 10^{-5} x^2 - 0{\cdot}68205 \times 10^{-8} x^3 \qquad (2)$$

For benzene-1, 2-dichloroethane system:

$$d = 1{\cdot}23803 - 0{\cdot}42966 \times 10^{-2} x - 0{\cdot}67177 \times 10^{-5} x^2 - 0{\cdot}77974 \times 10^{-8} x^3 \qquad (3)$$

with x = mole percentage of benzene

The specific volumes of pure liquids and their mixtures are determined at 30° C, 35° C, 40° C, 45° C and 50° C using the dilatometer. The densities are fitted by the method of least squares to the equation

$$d = a_1 + b_1 t + c_1 t^2 + d_1 t^3, \qquad (4)$$

TABLE III

Volume change of mixing for benzene-carbon tetrachloride system

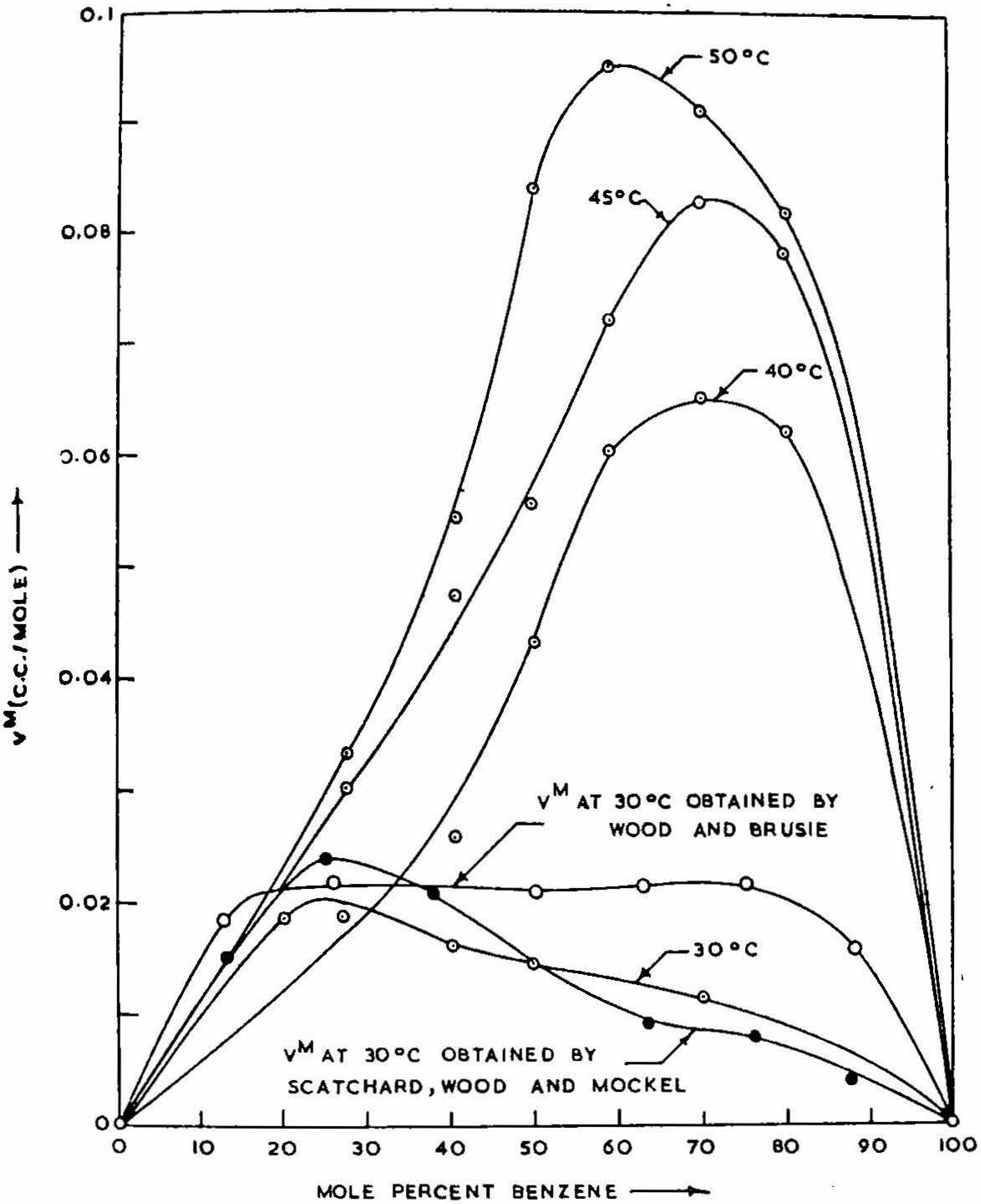
Mole Fraction of benzene, X_1	V^M Cm^3/mole
Temperature = 30° C	
0·09833	0·01909
0·2008	0·01889
0·4027	0·01597
0·4966	0·01474
0·6999	0·01148
Temperature = 35° C	
0·2775	0·00421
0·4049	0·02090
0·4988	0·04354
0·5906	0·06462
0·7022	0·06997
0·8043	0·07358
0·8974	0·08530
Temperature = 40° C	
0·2029	0·00520
0·2775	0·01894
0·4049	0·02618
0·4988	0·04331
0·5906	0·06063
0·7022	0·06505
0·8043	0·06196
0·8974	0·06907
Temperature = 45° C	
0·2029	0·00350
0·2775	0·03021
0·4049	0·04747
0·4988	0·05580
0·5906	0·07219
0·7022	0·08301
0·8043	0·07931
Temperature = 50° C	
0·2775	0·03325
0·4049	0·05343
0·4988	0·08402
0·5906	0·09510
0·7022	0·09104
0·8043	0·08240

The density at 30° C is found from equation (4) and used together with the density composition relationship at 30° C to calculate the composition of the liquid in the dilatometer. It is estimated that density and volume of mixing are accurate to 0·05% and 2·5% respectively. The volume change of mixing for benzene-carbon tetrachloride and benzene-1, 2-dichloroethane are presented in Tables III and IV and in graphical form as Figs. 3 and 4. The values of V^M for benzene-carbon tetrachloride are also determined by

TABLE IV

*Volume change of mixing for benzene-*1, 2-*dichloroethane system*

Mole fraction of benzene, x_1	V^M Cm³/mole
Temperature = 30° *C*	
0·1024	0·12740
0·2070	0·18726
0·4086	0·24423
0·4315	0·24785
0·6048	0·25124
0·7067	0·22728
0·8029	0·18969
0·9018	0·11536
Temperature = 35° *C*	
0·1028	0·11872
0·3073	0·22584
0·4089	0·24987
0·7044	0·22216
Temperature = 40° *C*	
0·1028	0·11668
0·3073	0·22315
0·4089	0·23827
0·7044	0·22224
Temperature = 45° *C*	
0·1028	0·11337
0·3073	0·22006
0·4089	0·23492
0·7044	0·21215
Temperature = 50° *C*	
0·1028	0·10246
0·3073	0·21402
0·4089	0·23381
0·7044	0·21730



FIG, 3. Mole Per cent Benzene *vs.* Volume of Mixing Benzene-Carbon Tetrachloride System

Wood and Brusie [1] and by Scatchard *et al.* [5]. The curves for 1, 2-dichloroethane system show that there is hardly any change in volume of mixing with temperature.

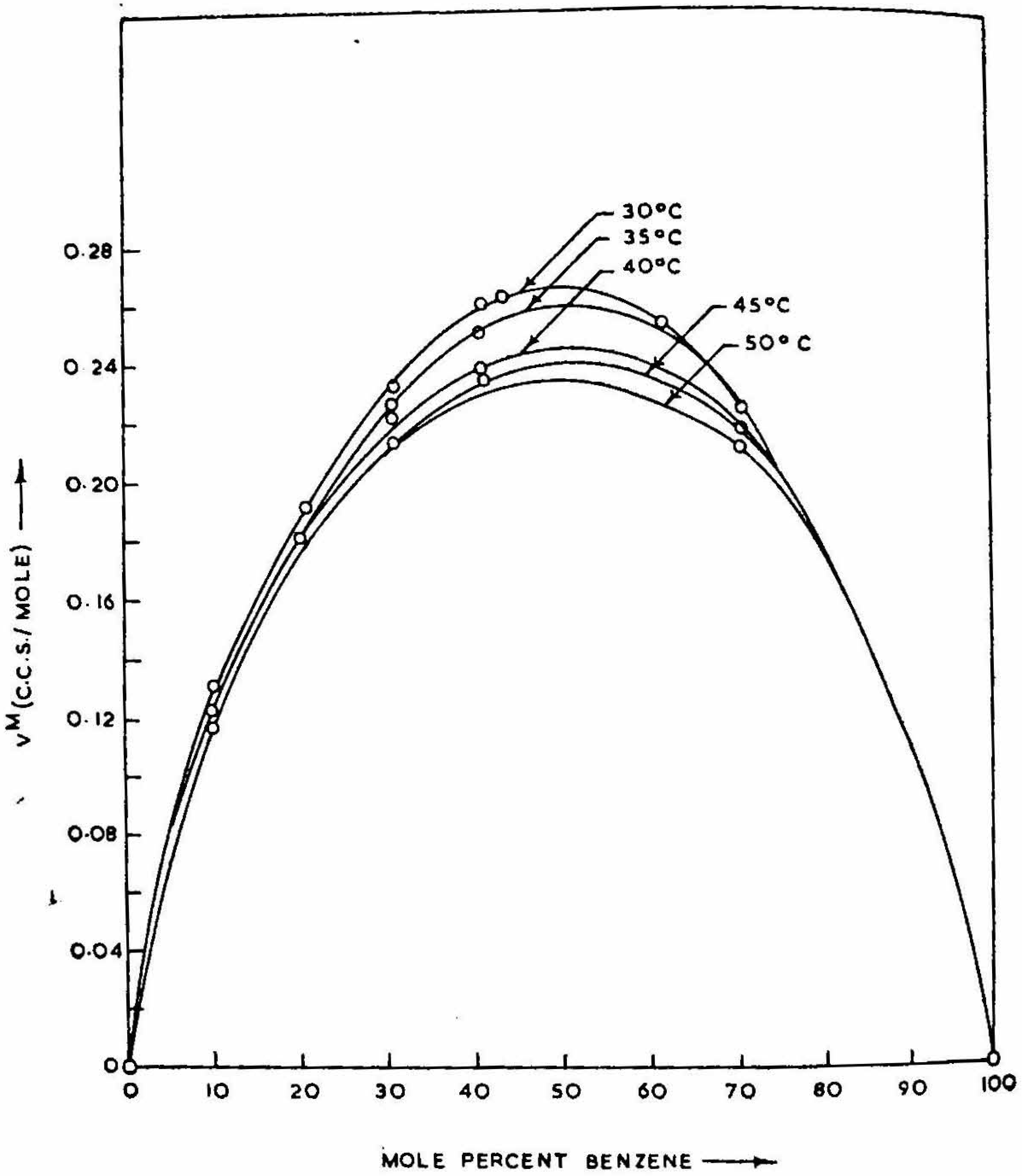


FIG. 4. Mole Per cent Benzene *vs.* Volume of Mixing. Benzene-1, 2-Dichloroethane System.

6. COMPARISON OF VOLUME CHANGE PREDICTED BY THEORIES OF SOLUTIONS WITH EXPERIMENTAL DATA

The systems chosen for comparison are;

(i) benzene-cyclohexane,

(ii) cyclohexane-carbon tetrachloride, and

(iii) benzene-1, 2-dichloroethane.

According to the cell model theory, the excess volume of mixing is given by [6, 7] the expression:

$$\begin{aligned}\frac{\gamma V^E}{(r_{AA}^*)^3} &= 0{\cdot}9161\,[4{\cdot}125\rho^2 + 0{\cdot}75\rho\delta + 1{\cdot}50\rho\theta\,(x_A - x_B)]\,x_A x_B \\ &\quad + 2{\cdot}032\,\frac{KT}{\Lambda_{AA}}\,[-\,2\theta - 0{\cdot}75\delta^2 + \theta\delta\,(1 + 2x_B) + \theta^2 \\ &\quad - 10{\cdot}44\rho^2 - 3\rho\theta - 2{\cdot}55\rho\theta\,(x_A - x_B) + 0{\cdot}227\rho\theta]\,x_A x_B \end{aligned} \tag{8}$$

where, γ is related to the distance between first neighbours 'a' by

$$a^3 = \gamma V \tag{9}$$

and

$$\rho = (r_{BB}^* - r_{AA}^*)/r_{AA}^* \tag{10}$$

$$\Lambda_{ij} = Z \mid \epsilon_{ij}^* \mid \tag{11}$$

$$\delta = \frac{1}{\Lambda_{AA}}\,[\Lambda_{BB} - \Lambda_{AA}] \tag{12}$$

$$\theta = \frac{1}{\Lambda_{AA}}\left[\Lambda_{AB} - \left(\frac{\Lambda_{BB} + \Lambda_{AA}}{2}\right)\right] \tag{13}$$

According to the average potential model theory, the excess volume of mixing is given by the expression [8]

$$\begin{aligned}\frac{V^E}{x_A x_B} &= \frac{3}{2}\,V_{AA}\rho\left[\theta\,(x_A - x_B) + \frac{\delta}{2} + \frac{11\rho}{4}\right] + TV_{AA}{}^1 \\ &\quad \times \Big[-\,2\theta + 9\rho^2 + \theta^2 - \frac{3}{4}\,\delta^2 + \theta\delta\,(1 + 2x_B) \\ &\quad - 3\rho\theta + \frac{9}{4}\,\rho\delta + \frac{3}{2}\,\rho\theta\,(x_A - x_B)\Big] + \frac{1}{2}\,T^2\,V_{AA}{}^{11} \\ &\quad \times \left[\theta^2 - \frac{3}{4}\,\delta^2 + \theta\delta\,(1 + 2x_B)\right] \end{aligned} \tag{14}$$

where,

$$V_{AA}{}^1 = \frac{dV_{AA}}{dT} \tag{15}$$

$$V_{AA}{}^{11} = \frac{d^2\,V_{AA}}{dT^2}\,. \tag{16}$$

In deriving the above equations, the following basic assumptions are involved:

(i) the translational partition function can be handled classically,

(ii) the internal partition function is independent of volume per molecule,

(iii) the interaction energy between molecules at a distance γ may be expressed in the form:

$$\epsilon_{ij}(r) = 4\epsilon_{ij}^*\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{17}$$

where,

$$\sigma = r_{ij}^* \, 2^{-1/6}, \tag{18}$$

(iv) random mixing is assumed

(v) $r_{AB}^* = \frac{1}{2}(r_{AA}^* + r_{BB}^*)$. (19)

In addition to these assumptions, the following assumptions are made for the purpose of calculations.

(i) $\theta = -\dfrac{\delta^2}{8}$.

(ii) Face-centered cubic lattice is assumed (this assumption is used only for the cell model equation). Hence, in this case, $Z = 12$ and $r = 1{\cdot}414$. The values of ϵ^* and σ used in this work are given in Table V. The values of δ and ρ calculated using the values ϵ^* and σ are presented in Table VI. The values of V_{AA}, $V_{AA}{}^1$ and $V_{AA}{}^{11}$ given by Prigogine *et al.* [10] are used in the present work. These values are given in Table VII.

TABLE V

Values of (ϵ/K) *and* σ [9]

Substance	ϵ/K °K	σ (Å)
Carbon tetrachloride	327	5·881
Cyclohexane	324	6·093
Benzene	440	5·270
1,2-dichloroethane	406	4·759

TABLE VI

Values of δ and ρ

System		δ	ρ
Cyclohexane-carbon tetrachloride :			
(i) Cyclohexane as reference	..	0·0	−0·035
(ii) Carbon tetrachloride as reference	..	0·0	0·036
Cyclohexane-benzene :			
(i) Cyclohexane as reference	..	0·015	−0·085
(ii) Benzene as reference	..	−0·015	0·093
Benzene-1,2-dichloroethane :			
(i) Benzene as reference	..	−0·077	—0·097
(ii) 1, 2-dichloroethane as reference	..	0·084	0·106

TABLE VII

Values of V_{AA}, V_{AA}^{1} and V_{AA}^{11} [10]

System		V_{AA} cm^3	V_{AA}^{1} cm^3/deg	V_{AA}^{11} cm^3/deg^2
Carbon tetrachloride	..	97·08	0·119	0·0002
Cyclohexane	..	108·74	0·132	0·0003

Using these values for the parameters, volume changes for different compositions at 30° C are calculated from the two equations and are compared with experimental data available in the literature. For benzene cyclohexane system, the values reported by Wood and Austin [11] and for cyclohexane-carbon tetrachloride system, the values reported by Wood and Gray [12] are used for comparison. Values of V^M predicted by cell model theory for benzene-1, 2-dichloroethane system are compared with the results of the present work.

The graphs for the systems benzene-cyclohexane, cyclohexane-carbon tetrachloride and benzene-1, 2-dichloroethane are shown as Figs. 5, 6 and 7 respectively. From the curves, it is seen that the predicted values and

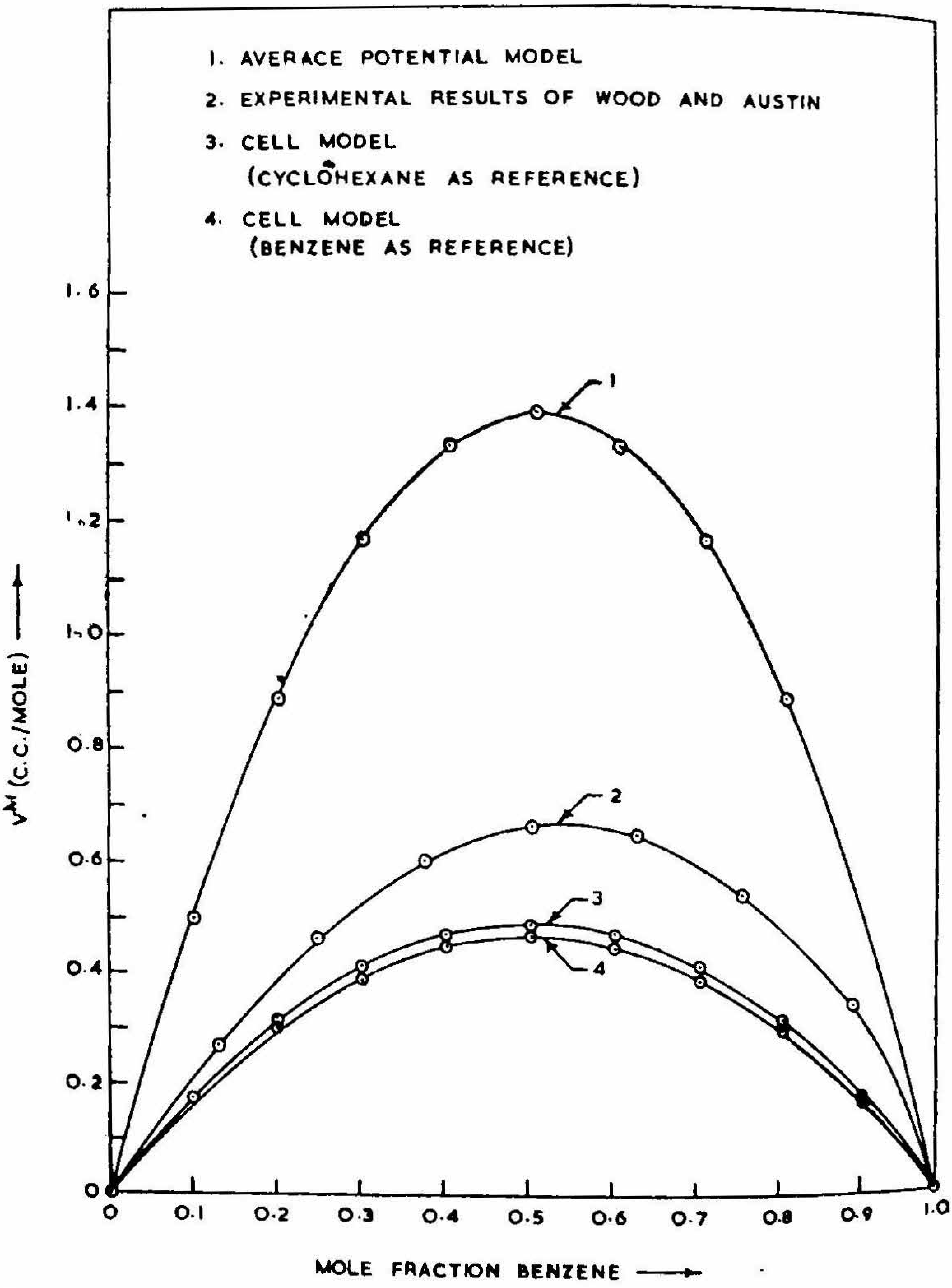


FIG. 5. Mole Fraction Benzene *vs.* Volume of Mixing at 30° Benzene-Cyclohexane System.

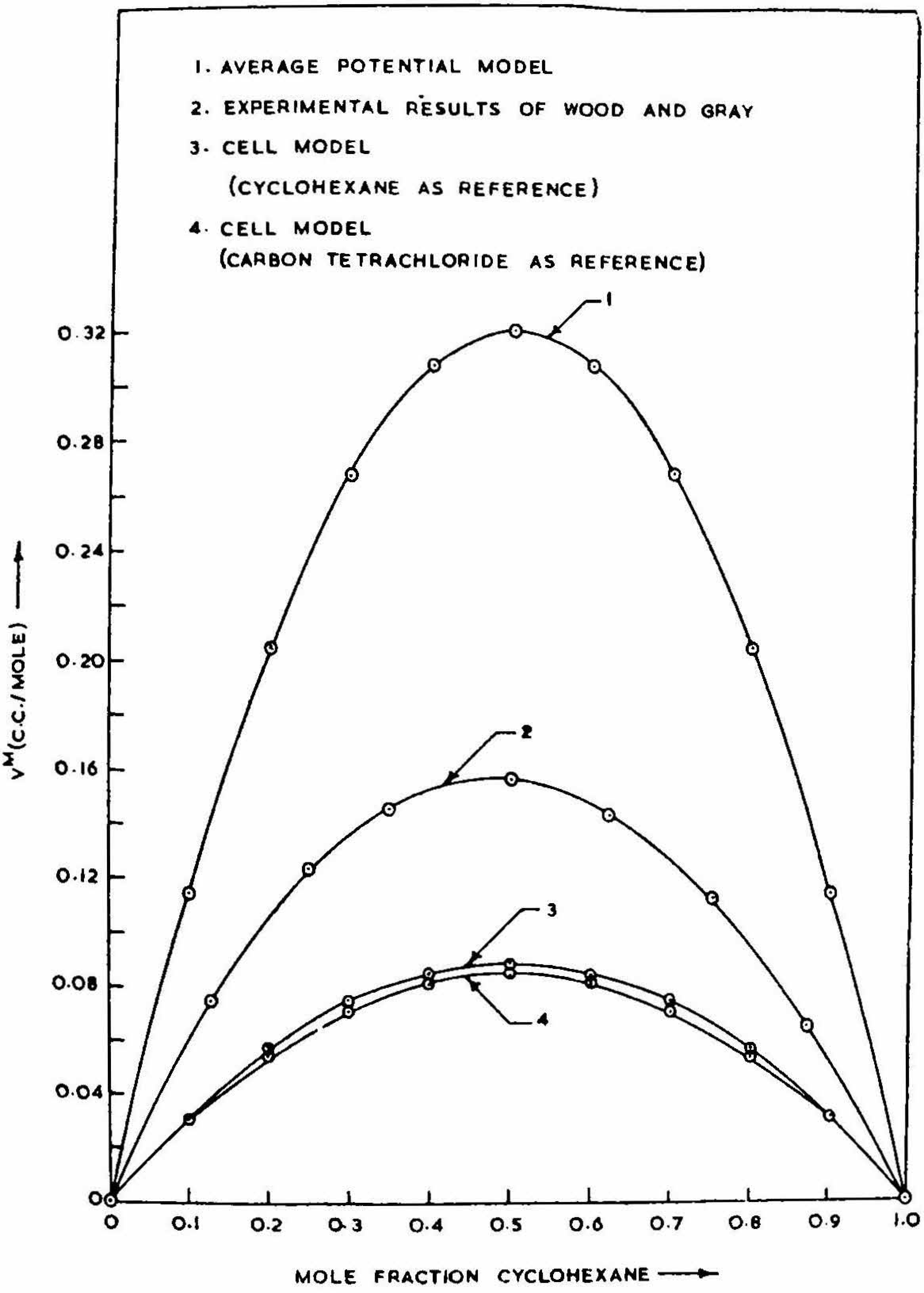


FIG. 6. Mole Fraction Cyclohexane *vs.* Volume of Mixing at 30° C Cyclohexane-Carbon Tetrachloride System.

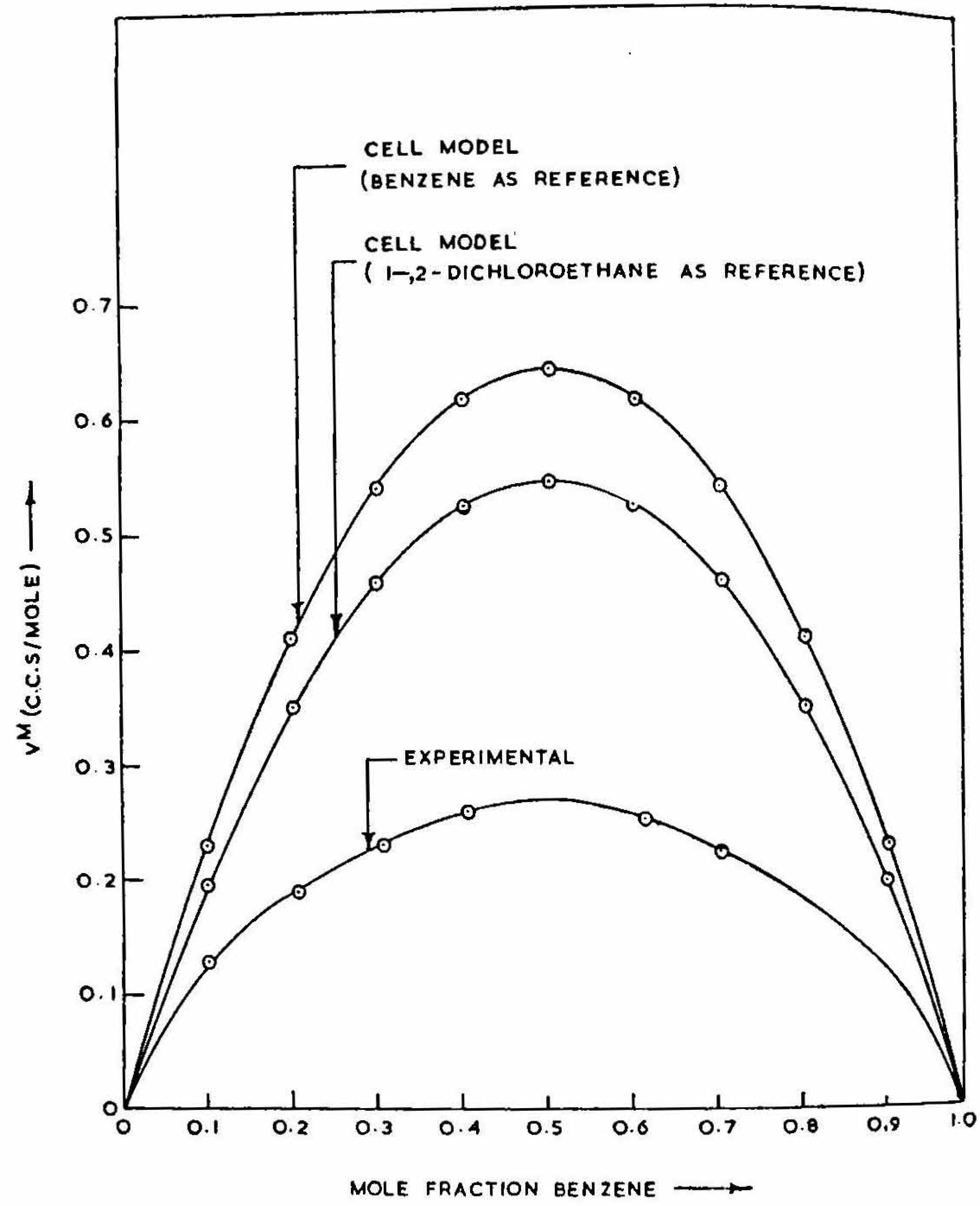


FIG. 7. Mole Fraction Benzene *vs.* Volume of Mixing at 30° C. (Benzene-1-, 2-Dichloroethane System)

actual values have the same sign and order of magnitude. Apparently, the cell model seems to conform more to the experimental values, but this may be due to the inaccuracy of the values of V_{AA}, V_{AA}^{1} and V_{AA}^{11} used in average potential model equation. Theoretically, the cell model is less satisfactory, because, besides the assumption it shares with the average potential theory, it uses some supplementary assumptions and simplifications (cell field, limits of cell, etc.) which are eliminated in the average potential model. From the results, we can come to the following conclusions:

(i) As far as prediction of volume change is concerned, the average potential model does not give any substantial improvement over the cell model.

(ii) To check the validity of any theory of solutions, it is necessary to compare thermodynamic functions of mixing other than volume change of mixing like excess entropy, excess free energy, etc., with experimental values. Mere comparison of volume change of mixing does not give a true picture.

NOMENCLATURE

a	Distance between first neighbours in the lattice assumed
d	Density gm/cm^3
K	Boltzman's constant
N	Avogadro's number
r	Distance between two molecules under consideration, Å
$r_{ij}{}^*$	Distance between two molecules i and j when the energy of interaction between them is minimum
T	Temperature, °K
V	Volume, cm^3/mole
V^1	Volume/molecule
V^0	Additive volume assuming no volume change on mixing
V_i^0	Volume/molecule for pure component i
V_{AA}	Volume, cm^3/mole for pure component A used as the reference substance
x	Mole fraction
Z	Co-ordination number for the lattice assumed
γ	A geometric factor depending on the lattice assumed [Equation (9)]
ρ	As defined in Equation (10)
$\epsilon_{ij}{}^*$	Force of interaction between molecules i and j [Equation (17)]
ϵ/K	Parameter in Lennard-Jones Potential, °K

Λ_{ij}	As defined in Equation (11)
δ	As defined in Equation (12)
θ	As defined in Equation (13)
σ	Collision diameter, Å [Equation (18)]

Superscripts :

E	Excess function
M	Describes thermodynamic functions of mixing

Subscripts :

1	Refers to benzene
2	Component other than benzene.

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