# Effect of Size and Shape in Binary Nonelectrolyte Solution
# I. Measurement of Excess Free Energy and Excess Volume of Benzene–Cyclooctane and Toluene–Cyclooctane

**Ramesh C. Mitra, Suhas C. Guhaniyogi, and Sailendra N. Bhattacharyya**[1]
*Department of Physical Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta-32, India*

**The excess free energies of the systems benzene–cyclooctane and toluene–cyclooctane have been measured over the entire mole fraction range using an all-glass mercury static equilibrium still at 25°, 40°, and 55°C. The excess volumes of the systems have also been measured over the entire mole fraction range at 40°C by precision pycnometry. The data were processed following the method of Scatchard et al. (1964).**

Direct measurement of the characteristic excess properties of binary nonelectrolyte mixtures, where the differences in molecular size, shape, volatility, and other physical properties of the components are maximal, has gained much importance in recent years. In keeping with this trend, we present the results of our full-scale measurements of the excess free energies by the static equilibrium method as well as the excess volumes for the systems benzene-cyclooctane and toluene–cyclooctane. For both systems, reliable excess enthalpy data have been tabulated by McLure et al. *(2)*. A correlation of the excess free energies and excess volumes with excess enthalpies of the mixtures and a systematic application of the current theories of solution have been made and will be published later.

## Experimental

The static equilibrium still constructed in this laboratory has been described in full detail *(3)* along with studies on the excess properties of the benzene–cyclohexane system, and they are in good agreement with the results obtained by Scatchard et al. *(6)* with a circulating-type still.

Although the still used in the present work was similar in many aspects to that described by Scatchard and Satkiewiez *(4)*, it was of all-glass mercury surface in an easy-to-handle design. It was an integrated type of apparatus with provisions for degassing and storage of the components in an isolated condition and could be operated smoothly over a variety of component characteristics.

As usual with such stills, the equilibrium pressures of the mixture at each of a series of temperatures were balanced with an inert gas pressure applied from a manostat using a null-type mercury manometer. The manostat pressure was then measured with an arrangement described previously *(1)*, the only difference being that a straight-limbed U-tube was used for pressures lower than 100 mm and that separate illuminating arrangements were made for each limb besides usual thermostating provisions which kept the temperature constant within ±0.01°C. An invar scale cathetometer, calibrated by the National Physical Laboratory (India), was used and the usual corrections for temperature and *g*-values were employed. The overall precision attained in the measurement of pressure was ±0.01 mm Hg.

Temperature of the static equilibrium was measured by a five-junction copper-constantan thermocouple with the cold junction immersed securely in an ice-water bath. The couple was previously calibrated in situ using the vapor pressure of pure benzene at each of the experimental temperatures and using the well-known Antoine equation. A Leeds & Northrup $K_2$-type potentiometer was used for temperature measurements with a precision of ±0.002°C.

An accurate determination of the overall composition of the equilibrium mixture was made after distilling off all of the mixture, thorough stirring with a magnetic stirrer, and then drawing off a portion of it as a representative sample with a hypodermic syringe inserted directly into the pycnometer. Using the method of Scatchard *(4)*, the liquid phase was made up gravimetrically to known composition, and the vapor phase was computed by use of thermodynamic equations, since the mixture was thoroughly degassed.

The densitometric technique used in the present work has been given in detail elsewhere *(1)*. The single-tube pycnometers were of about 4-ml capacity. A semimicro Mettler balance with a calibration of its weights and of the optical scale against its own weights was used for the weighings. The pycnometer bath was kept at a constant temperature of 40° ± 0.002°C. Heights of the liquid columns and of the menisci were read by using an invar scale traveling microscope. The readings were corrected for buoyancy of air, and temperature, pressure, and humidity of the balance room.

The mixing pycnometers were of 10-ml capacity and a magnetic stirrer was used to ensure uniform mixing. Corrections were applied for the vapor of the first component expelled on injecting the second one. The results of density measurements were found to differ by only several parts in $10^5$ from the literature values in the case of pure components.

The volume change data obtained from measurements on the pure components and those of the mixtures made up gravimetrically to known compositions were used for determining the compositions of the unknown samples from the equilibrium still.

The following empirical relation was used to express the density and composition of the mixture in terms of the mole fraction of the more volatile component as

$$\kappa_1 = \alpha\xi + \beta\xi(1-\xi) + \gamma\xi(1-\xi)(1-2\xi) + \delta\xi(1-\xi)(1-2\xi)(1-3\xi) \quad (1)$$

where

$$\xi = (\rho_1 - \rho_{\text{mix}})/(\rho_1 - \rho_2) \quad (2)$$

and $\rho$ represents density with the appropriate suffix.

The mole fractions calculated on the basis of Equation 1 were used to plot the deviation $\delta x$ in mole fraction against $x$ the mole fraction itself, and using $x = x_{\text{calcd}}$ in the first approximation the deviation in $x$ was evaluated from the smooth curve. This plot was finally used to correct the mole fractions, and the deviation in mole fractions was of the order of 1 in $10^5$.

---

[1] To whom correspondence should be addressed.

The values of $V^E$ at 40°C, so obtained, were smoothed with the help of an equation of the form,

$$V^E = x_1x_2 \sum_{n=0}^{4} An(x_1 - x_2)^n \tag{3}$$

where the values of the constants are listed in Table I.

### Purifications of the Samples

Benzene and toluene used in this work were E. Merck A. R. Grade. The Cyclooctane used was also A. R. quality obtained from Aldrich Chemical Co.

All the samples were thoroughly treated with concentrated sulfuric acid, washed until neutral, and dried. Finally, each sample was fractionated in a 40-theoretical-plate fractionating column and only the middle fraction was accepted in each case. All conventional procedures were followed in the purification of mercury and water used.

### Degassing

Each pure component was subjected to meticulous degassing by a timed programmer, with an evacuating pump connected to the vapor space. A 2-ft column packed with ¼-in. Raschig rings was fitted above each storage flask, and no liquid was allowed to "age" during the experiment. The temperature of the still was maintained by helical mercury-toluene thermoregulators and nonmechanical thyratron relays. Other constructional and operational details have been reported elsewhere *(3)*. The present experiments for $G^E$ were carried out at 25°, 40°, and 55°C and for $V^E$ at 40°C only.

### Results

The data were analyzed using the method of Scatchard and Satkiewicz *(4)*.

Introducing two temperature-dependent parameters, *a* and *b*, Scatchard has given the following equation for the excess free energy of the mixture (1, 2) at an absolute temperature *T:*

$$\frac{G^E}{RT} = -x_1 \ln(1 - ax_2) - x_2 \ln(1 - bx_1) \tag{4}$$

where $x_i$ are the liquid-phase mole fraction ($i$ = 1,2). The corresponding partial molar quantities are given by

$$\frac{G_1^E}{RT} = -\ln(1 - ax_2) + x_2\text{\textcircled{H}} \tag{5}$$

$$\frac{G_2^E}{RT} = -\ln(1 - bx_1) - x_1\text{\textcircled{H}} \tag{6}$$

where

$$\text{\textcircled{H}} = \frac{ax_2}{1 - ax_1} - \frac{bx_1}{1 - bx_2} \tag{7}$$

The total pressure is

$$p = p_1x_1 \exp\left(\frac{G_1^E}{RT} + \delta_1\right) + p_2x_2 \exp\left(\frac{G_2^E}{RT} + \delta_2\right) \tag{8}$$

and the vapor-phase mole fraction is given by

$$y_2 = \frac{p_2x_2 \exp(G_2^E + \delta_2)}{p} \tag{9}$$

where $\delta_i - s$ are the correction terms due to nonideality of the vapor

$$-\delta_1 = [(\beta_{11} - \bar{v}_1)(p - p_1) + (2\,\delta_{12} - \delta_{11} - \delta_{22})py_2^2]/RT \tag{10}$$

$$-\delta_2 = [(\beta_{22} - \bar{v}_2)(p - p_2) + (2\,\delta_{12} - \delta_{11} - \delta_{22})py_1^2]/RT \tag{11}$$

where $\bar{v}_i - s$ are the molar volumes and $\beta_{ij}$, the second virial coefficients of the pure components ($i = j$) or of the mixture ($i \neq j$).

The successive approximation method developed by Scatchard and Satkiewicz *(4)* was used in the present analysis. By taking the overall composition, *Z*, at the lowest temperature as the liquid-phase composition and by neglecting virial corrections—i.e., $Z_2 \rightarrow x_2$ and $\delta_1 \simeq 0 \simeq \delta_2$—Equation 8 was fitted by adjusting to a set of values for $(a,b)$. By use of this as the first approximation, rough values of $y_2$ were obtained using Equation 9. This set of $x_2$ and $y_2$ was then used to arrive at a better $x_2$ by gravimetric correction and so on until consistency was reached. This value of $x_2$ then served as the starting approximation at the next higher temperature and so on. Thus at each temperature a single set of $(x,y)$, $(a,b)$, and $p$ was obtained which gave $G^E$ and $(a,b)$ as smooth functions of temperature.

Benzene-cyclooctane: $a = 2.626713 - 15.333 \times 10^{-3}\,T + 26.67 \times 10^{-6}\,T^2$
$b = 2.31129 + 20.4995 \times 10^{-3}\,T - 33.44 \times 10^{-6}\,T^2$

Toluene-cyclooctane: $a = 0.944331 - 3.025 \times 10^{-3}\,T + 2.222 \times 10^{-5}\,T^2$
$b = 1.022411 - 4.05 \times 10^{-3}\,T + 4.444 \times 10^{-6}\,T^2$

The mixed virial coefficients were obtained using the equation given by Scatchard and Ticknor *(5)* and are shown in Table II.

$$\beta_{ij} = B_{ij} - \frac{A_{ij}}{T^2} \tag{12}$$

where

$$B_{ij} = \tfrac{1}{8}\,(B_{ii}^{1/3} + B_{jj}^{1/3})^3 \tag{13}$$

**Table I. Values of Constants for Excess Volume Equation 3**

| | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $A_4$ |
|---|---|---|---|---|---|
| Benzene-cyclooctane | 2.304 | −0.013021 | −0.054697 | −0.455729 | +0.169297 |
| Toluene-cyclooctane | 2.116 | +0.213543 | −0.003911 | +0.390622 | +0.514336 |

**Table II. Virial Coefficients, Ml Mol$^{-1}$**

| Benzene-cyclooctane | | | | Toluene-cyclooctane | | | |
|---|---|---|---|---|---|---|---|
| *t*, °C | $-\beta_{11}$ | $-\beta_{22}$ | $-\beta_{12}$ | *t*, °C | $-\beta_{11}$ | $-\beta_{22}$ | $-\beta_{12}$ |
| 25 | 1379.1 | 2843.1 | 2015.46 | 25 | 1980.14 | 2843.1 | 2379.93 |
| 40 | 1243.7 | 2567.2 | 1818.89 | 40 | 1786.77 | 2567.2 | 2148.42 |
| 55 | 1125.5 | 2328.2 | 1648.66 | 55 | 1619.42 | 2328.2 | 1947.92 |

and

$$A_{ij} = \left(\frac{B_{ij}^2}{B_{ii}B_{jj}}\right)(A_{ii}A_{jj})^{1/2} \tag{14}$$

where $i = j$ for a pure liquid and $i \neq j$ for a mixture.

Further, using Equation 4 with the classical relation,

$$H^E = G^E - T\,\frac{dG^E}{dT} \tag{15}$$

one gets

$$H^E = -RT^2x_1x_2\left[\frac{1}{1 - ax_2}\,\frac{da}{dT} + \frac{1}{1 - bx_1}\,\frac{db}{dT}\right] \tag{16}$$

This relation was used to calculate $H^E$ from $G^E$ data.

The smoothed values of $V^E$ at 40°C are shown in Table III for both the systems studied. The corresponding densities of the mixture and deviations between the experimental and theoretical values of mole fractions are also shown. Plots of the excess volumes against mole fractions are shown in Figure 1. For the benzene-cyclooctane system, the equimolar $V^E$ is 0.578 ml/mol, and the peak has a slight tendency to shift toward the benzene-rich concentrations. For the toluene-cyclooctane system, however, there is better symmetry, and the peak value of 0.532 ml/mol occurs at a mole fraction between 0.5 and 0.51 of cyclooctane.

The deviations $\Delta P$ between the observed and calculated pressures and the corresponding liquid- and vapor-phase mole fractions obtained by Wilson's method are shown in Tables IV and V, respectively. The average deviation in the values of $\Delta P$ is only several parts per thousand. The corresponding values of log $(\alpha_{12}p_2{}^0/p_1{}^0)$ are also given as a test of thermodynamic consistency.

The values of $G^E$ obtained at rounded mole fraction by fitting Scatchard's biparametric Equation 4 have also been plotted against mole fraction at all three temperatures studied for both systems in Figures 2*a*, and *b*. For

**Table III. Excess Volumes of Mixing**

| $x_2$ | $\rho_{\text{mix}}$, gram ml$^{-1}$ | $V^E$, ml mol$^{-1}$ | $\delta x = x_{2\text{ calcd}} - x_{2\text{ exptl}}$ |
|---|---|---|---|
| | Benzene–cyclooctane | | |
| 0.00000 | 0.85766 | 0.000 | |
| 0.07901 | 0.85163 | 0.190 | 0.00000 |
| 0.14110 | 0.84756 | 0.292 | +0.00053 |
| 0.22420 | 0.84372 | 0.434 | +0.00035 |
| 0.30546 | 0.83871 | 0.498 | −0.00006 |
| 0.41079 | 0.83413 | 0.555 | −0.00003 |
| 0.48123 | 0.83147 | 0.572 | 0.00000 |
| 0.58830 | 0.82809 | 0.560 | +0.00026 |
| 0.68581 | 0.82546 | 0.524 | +0.00026 |
| 0.77862 | 0.82347 | 0.372 | −0.00043 |
| 0.92113 | 0.82106 | 0.143 | 0.00000 |
| 1.00000 | 0.81995 | 0.000 | |
| | Toluene–cyclooctane | | |
| 0.00000 | 0.84742 | 0.000 | |
| 0.11330 | 0.84214 | 0.196 | +0.00004 |
| 0.20999 | 0.83814 | 0.327 | 0.00000 |
| 0.30715 | 0.83452 | 0.430 | +0.00003 |
| 0.37993 | 0.83208 | 0.421 | −0.00007 |
| 0.50122 | 0.82851 | 0.532 | 0.00000 |
| 0.62984 | 0.82538 | 0.507 | −0.00003 |
| 0.79432 | 0.82228 | 0.389 | 0.00000 |
| 0.87909 | 0.82095 | 0.278 | +0.00005 |
| 1.00000 | 0.81995 | 0.000 | |

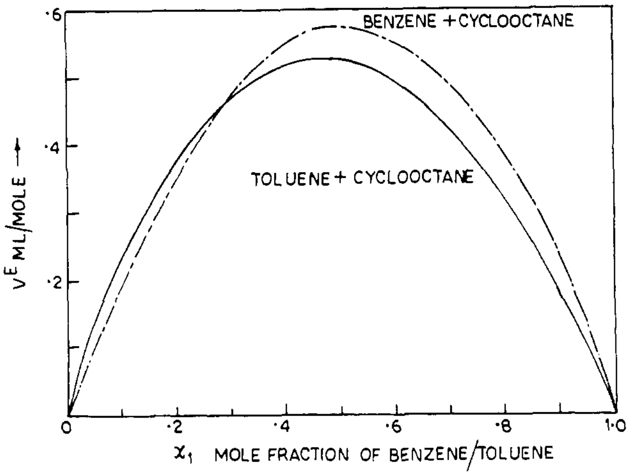

**Figure 1.** Plot of $V^E$ at 40°C against mole fractions of benzene-toluene for benzene-cyclooctane and toluene-cyclooctane systems

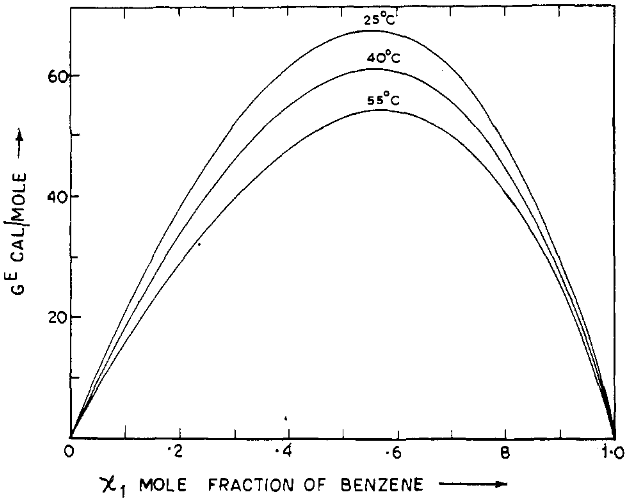

**Figure 2*a*.** Plot of $G^E$ at 25°C, 40°C, and 55°C against mole fractions of benzene for benzene-cyclooctane system

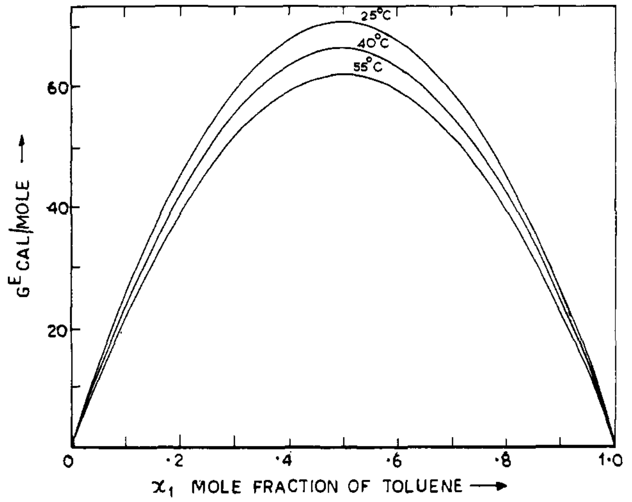

**Figure 2*b*.** Plot of $G^E$ at 25°C, 40°C, and 55°C against mole fractions of toluene for toluene-cyclooctane system

**Table IV. Equilibrium Pressures, Measured in mm Hg**

Benzene–cyclooctane

| $t$, °C \ $z_2$ | 0 | 0.0782 | 0.1425 | 0.2403 | 0.3164 | 0.4371 | 0.4751 | 0.5088 | 0.5202 | 0.6490 | 0.7260 | 0.8388 | 1.0 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $P_{\text{meas}}$ | | | | | | | | | | | | | |
| 25 | 95.18 | 88.82 | 84.00 | 77.29 | 71.73 | 62.66 | 59.92 | 57.43 | 56.24 | 45.02 | 36.83 | 24.62 | 5.81 |
| 40 | 182.79 | 170.37 | 161.08 | 148.81 | 137.55 | 119.81 | 113.85 | 109.26 | 107.25 | 85.65 | 70.52 | 47.30 | 12.95 |
| 55 | 326.72 | 307.31 | 288.57 | 266.22 | 246.54 | 213.86 | 203.76 | 194.90 | 191.16 | 152.57 | 125.93 | 86.10 | 27.41 |
| $\Delta P = (P_{\text{meas}} - P_{\text{calcd}})$ in mm Hg | | | | | | | | | | | | | |
| 25 | | −0.10 | −0.14 | +0.15 | +0.03 | −0.09 | +0.14 | +0.36 | +0.12 | +0.09 | −0.68 | −0.92 | |
| 40 | | −0.53 | −0.65 | +0.64 | +0.01 | −0.18 | −0.34 | +0.35 | +0.13 | +0.27 | −0.70 | −1.51 | |
| 55 | | +1.43 | −1.09 | +0.83 | +0.35 | −0.49 | −0.04 | +0.66 | +0.38 | +0.54 | −1.06 | −1.93 | |

Toluene–cyclooctane

| $t$, °C \ $z_2$ | 0 | 0.0937 | 0.1790 | 0.2673 | 0.2896 | 0.3990 | 0.4338 | 0.4839 | 0.5461 | 0.6437 | 0.7614 | 0.8740 | 1.0 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $P_{\text{meas}}$ | | | | | | | | | | | | | |
| 25 | 28.68 | 26.98 | 25.52 | 23.50 | 23.19 | 21.17 | 20.57 | 19.63 | 18.50 | 16.39 | 13.52 | 9.96 | 5.81 |
| 40 | 59.31 | 56.34 | 52.43 | 49.07 | 48.00 | 43.68 | 42.53 | 40.55 | 37.92 | 34.07 | 28.25 | 21.31 | 12.95 |
| 55 | 114.14 | 108.48 | 101.66 | 94.86 | 90.81 | 84.96 | 82.40 | 78.90 | 74.08 | 65.92 | 55.72 | 42.46 | 27.41 |
| $\Delta P = (P_{\text{meas}} - P_{\text{calcd}})$ in mm Hg | | | | | | | | | | | | | |
| 25 | | +0.06 | +0.15 | −0.28 | −0.19 | −0.22 | −0.17 | −0.15 | −0.04 | −0.05 | −0.06 | −0.36 | |
| 40 | | +0.63 | −0.09 | −0.17 | −0.40 | −0.59 | −0.39 | −0.39 | −0.40 | −0.02 | −0.02 | −0.46 | |
| 55 | | +1.08 | +0.30 | −0.27 | −0.73 | −0.70 | −0.49 | −0.41 | −0.36 | −0.40 | +0.30 | −0.95 | |

**Table V. Equilibrium Phase Compositions (Mole Fractions)**

Benzene–cyclooctane

| $t$, °C \ $z_2$ | 0.0782 | 0.1425 | 0.2403 | 0.3164 | 0.4371 | 0.4751 | 0.5088 | 0.5202 | 0.6490 | 0.7260 | 0.8388 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $x_2$ | | | | | | | | | | | |
| 25 | 0.07848 | 0.14287 | 0.24087 | 0.31720 | 0.43806 | 0.47608 | 0.50987 | 0.52149 | 0.65004 | 0.72707 | 0.83959 |
| 40 | 0.07863 | 0.14318 | 0.24137 | 0.31782 | 0.43880 | 0.47688 | 0.51068 | 0.52247 | 0.65086 | 0.72785 | 0.84015 |
| 55 | 0.07890 | 0.14365 | 0.24213 | 0.31878 | 0.43993 | 0.47811 | 0.51192 | 0.52396 | 0.65209 | 0.72902 | 0.84097 |
| $y_2$ | | | | | | | | | | | |
| 25 | 0.00811 | 0.01433 | 0.02374 | 0.03151 | 0.04604 | 0.05143 | 0.05698 | 0.05896 | 0.08786 | 0.11565 | 0.19275 |
| 40 | 0.00901 | 0.01599 | 0.02673 | 0.03579 | 0.05293 | 0.05945 | 0.06587 | 0.06830 | 0.10278 | 0.13560 | 0.22520 |
| 55 | 0.01029 | 0.01831 | 0.03081 | 0.04152 | 0.06202 | 0.06988 | 0.07762 | 0.08059 | 0.12199 | 0.16117 | 0.26467 |
| $\log (\alpha_{12}p_2^0/p_1^0)$ | | | | | | | | | | | |
| 25 | −0.1969 | −0.1553 | −0.0991 | −0.0600 | −0.0065 | +0.0096 | +0.0213 | +0.0257 | +0.0705 | +0.0943 | +0.1262 |
| 40 | −0.1775 | −0.1378 | −0.0861 | −0.0513 | −0.0041 | +0.0091 | +0.0203 | +0.0239 | +0.0615 | +0.0817 | +0.1073 |
| 55 | −0.1604 | −0.1223 | −0.0741 | −0.0427 | −0.0015 | +0.0099 | +0.0194 | +0.0226 | +0.0538 | +0.06996 | +0.09086 |

Toluene–cyclooctane

| $t$, °C \ $z_2$ | 0.09367 | 0.17895 | 0.26725 | 0.28955 | 0.39904 | 0.43380 | 0.48386 | 0.54611 | 0.64372 | 0.76139 | 0.87398 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $x_2$ | | | | | | | | | | | |
| 25 | 0.09374 | 0.17907 | 0.26743 | 0.28975 | 0.39929 | 0.43407 | 0.48414 | 0.54641 | 0.64402 | 0.76166 | 0.87417 |
| 40 | 0.09380 | 0.17917 | 0.26760 | 0.28993 | 0.39952 | 0.43431 | 0.48439 | 0.54667 | 0.64429 | 0.76190 | 0.87433 |
| 55 | 0.09390 | 0.17935 | 0.26786 | 0.29022 | 0.39989 | 0.43470 | 0.48479 | 0.54711 | 0.64473 | 0.76228 | 0.87458 |
| $y_2$ | | | | | | | | | | | |
| 25 | 0.03011 | 0.05675 | 0.08455 | 0.09174 | 0.12896 | 0.14179 | 0.16156 | 0.18902 | 0.24185 | 0.33501 | 0.49593 |
| 40 | 0.03120 | 0.05926 | 0.08888 | 0.09663 | 0.13681 | 0.15072 | 0.17220 | 0.20225 | 0.25902 | 0.35825 | 0.52427 |
| 55 | 0.03310 | 0.06322 | 0.09537 | 0.10376 | 0.14765 | 0.16290 | 0.18635 | 0.21889 | 0.28075 | 0.38638 | 0.55649 |
| $\log (\alpha_{12}p_2^0/p_1^0)$ | | | | | | | | | | | |
| 25 | −0.1707 | −0.1340 | −0.0965 | −0.0871 | −0.0412 | −0.0266 | −0.0058 | +0.01995 | +0.0603 | +0.10897 | +0.1555 |
| 40 | −0.1539 | −0.1212 | −0.0874 | −0.0792 | −0.0379 | −0.0249 | −0.0061 | +0.0163 | +0.0535 | +0.0974 | +0.1393 |
| 55 | −0.1369 | −0.1093 | −0.0792 | −0.0716 | −0.0345 | −0.0228 | −0.0059 | +0.01498 | +0.0478 | +0.0873 | +0.1253 |

**Table VI. Excess Quantities at Round Mole Fractions (Cal/Mol)**

|  |  |  |  |  | $x_1$ |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 |
|  |  |  |  |  | Benzene-cyclooctane |  |  |  |  |
| t, °C |  |  |  |  | $G^E$ |  |  |  |  |
| 25 | 20.70 | 38.11 | 51.87 | 61.60 | 66.80 | 66.91 | 61.23 | 48.93 | 28.96 |
| 40 | 18.11 | 33.55 | 45.96 | 54.95 | 60.02 | 60.58 | 55.90 | 45.08 | 26.94 |
| 55 | 15.39 | 28.75 | 39.73 | 47.95 | 52.92 | 54.00 | 50.44 | 41.22 | 25.00 |
|  |  |  |  |  | $H^E$ |  |  |  |  |
| 25 | 77.09 | 137.24 | 179.92 | 204.99 | 212.57 | 202.92 | 176.40 | 132.35 | 74.48 |
|  |  |  |  |  | Toluene-cyclooctane |  |  |  |  |
|  |  |  |  |  | $G^E$ |  |  |  |  |
| 25 | 25.74 | 45.62 | 59.70 | 68.06 | 70.76 | 67.82 | 59.27 | 45.13 | 25.37 |
| 40 | 24.13 | 42.79 | 56.03 | 63.91 | 66.47 | 63.73 | 55.71 | 42.41 | 23.85 |
| 55 | 22.49 | 39.90 | 52.28 | 59.66 | 62.07 | 59.53 | 52.05 | 39.64 | 22.29 |
|  |  |  |  |  | $H^E$ |  |  |  |  |
| 25 | 57.21 | 100.78 | 131.23 | 149.00 | 134.40 | 147.65 | 128.85 | 98.04 | 55.14 |

the system benzene-cyclooctane, they show an appreciable deviation from equimolar symmetry, reaching maxima of 67.5, 61.1, and 54.4 cal/mol, respectively, at 25°, 40°, and 55°C between 0.55 and 0.57 mole fractions of benzene. For the toluene-cyclooctane system, however, they are more symmetrical with peak values of 70.8, 66.5, and 62.1 cal/mol, respectively, at 25°, 40°, and 55°C at near-equimolar concentrations.

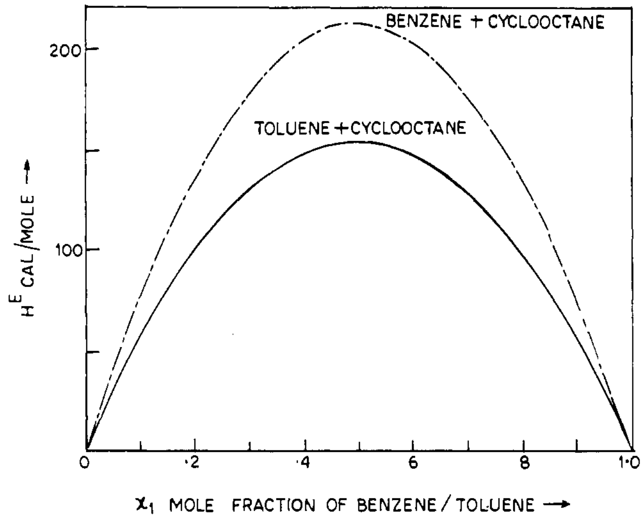

**Figure 3.** Plot of $H^E$ at 25°C against the mole fractions of benzene and toluene for the systems benzene-cyclooctane and toluene-cyclooctane, respectively

The values of $H^E$ at 25°C were calculated from the corresponding values of $G^E$ at rounded mole fractions (Table VI). They also showed good symmetry when plotted (Figure 3) for both the systems benzene-cyclooctane and toluene-cyclooctane and the peak values of 212.6 and 154.4 cal/mol were, respectively, 10% and 5% higher than the results of McLure et al. *(2)* obtained by direct calorimetric measurements. Such a difference is obviously due to the fact that even a small uncertainty in the values of $G^E$ over a given range of temperature produces much larger deviations in the values of $H^E$ obtained by such a method *(7)*. This method is therefore indicated for a qualitative idea of the heats of mixing when directly measured data are not readily available.

## Acknowledgment

Thanks are due to S. R. Palit, Department of Physical Chemistry, Indian Association for the Cultivation of Science, Calcutta.

## Literature Cited

(1) Bhattacharyya, S. N., Mukherjee, A., *J. Phys. Chem.*, **72**, 56 (1968).
(2) McLure, I. A., Bennett, J. E., Watson, A. E. P., Benson, G. C., *ibid.*, **69**, 2753 (1965).
(3) Mitra, R. C., Bhattacharyya, S. N., *Ind. J. Phys.*, **45**, 241 (1972).
(4) Scatchard, G., Satkiewicz, F. G., *J. Amer. Chem. Soc.*, **86**, 130 (1964).
(5) Scatchard, G., Ticknor, L. B., *ibid.*, **74**, 3724 (1952).
(6) Scatchard, G., Wilson, G. M., Satkiewicz, F. G., *ibid.*, **86**, 125 (1964).
(7) Williamson, A. G., Scott, R. L., *J. Phys. Chem.*, **65**, 275 (1961).

Received for review March 1, 1972. Accepted December 13, 1972. This work was supported by the C.S.I.R. Research Unit.