

**SURFACE TENSIONS AND SURFACE HEATS OF MIXING OF MIXTURES OF 1,2-DIBROMOETHANE WITH CYCLOHEXANE, BENZENE, TOLUENE, *o*-XYLENE, *m*-XYLENE, AND *p*-XYLENE AT 298.15, 303.15, AND 308.15 K**

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**ABSTRACT**

Surface tensions of mixtures of 1,2-dibromoethane+cyclohexane, benzene, +toluene, +*o*-xylene, +*m*-xylene, and +*p*-xylene have been measured as a function of composition at 298.15, 303.15 and 308.15 K. Interchange energies and surface heats of mixing in these mixtures were computed.

**INTRODUCTION**

Surface tensions of binary liquid mixtures have been treated theoretically by Butler<sup>1</sup>, Schuchowitsky<sup>2</sup>, Belton and Evans<sup>3</sup>, Guggenheim<sup>4</sup>, and Defay and Prigogine<sup>5</sup>. Guggenheim developed a statistical theory of surface tension of imperfect solutions for which limitations were worked out by Prigogine<sup>6</sup>. Prigogine and Englert-Chwoies<sup>7</sup> combined average potential model for interactions in the cell theory. Bellemans and Stecki<sup>8</sup> approach dispensed with the specifications of layers in which composition differed from the bulk phase. Surface tension data can be used to obtain important information regarding the surface properties. James et al.<sup>9</sup> have used surface entropy and surface heat of mixing to study the formation of complexes in binary mixtures. We measured surface tensions of the above-mentioned mixtures and the surface tension data have been analysed in the light of above approaches including Hildebrand model<sup>10</sup>.

**EXPERIMENTAL**

Cyclohexane, benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene (all B.D.H. grade) and 1,2-dibromoethane (Reidel) were purified as described earlier<sup>11,12</sup>. The purities of the samples were checked by measuring their densities; the results agreed to within  $0.00002 \text{ g cm}^{-3}$  with those in literature<sup>13,14</sup>.

The surface tensions were measured by the capillary rise method:

Uniform bore pyrex glass capillaries were fixed in a glass cell (specially designed for this purpose). Uniformity of the bore of capillary was checked by measuring the

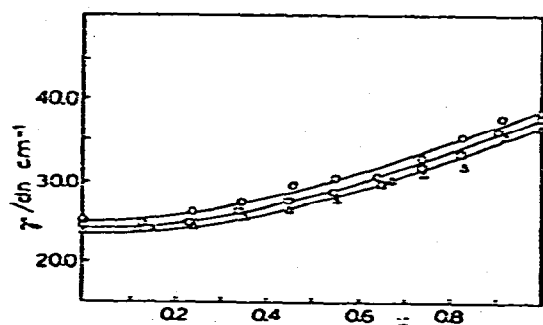


Fig. 1. Plot of surface tension  $\gamma$  against mole fraction  $x$  for the system  $x$  1,2-dibromoethane +  $(1-x)$  cyclohexane at 298.15, 303.15 and 308.15 K.  $\circ$ — $\circ$ , 298.15 K;  $\square$ — $\square$ , 303.15 K;  $\triangle$ — $\triangle$ , 308.15 K.

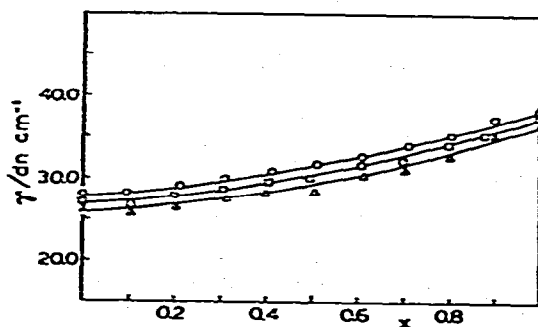


Fig. 2. Plot of surface tension  $\gamma$  against mole fraction  $x$  for the system  $x$  1,2-dibromoethane +  $(1-x)$  benzene at 298.15, 303.15 and 308.15 K.  $\circ$ — $\circ$ , 298.15 K;  $\square$ — $\square$ , 303.15 K;  $\triangle$ — $\triangle$ , 308.15 K.

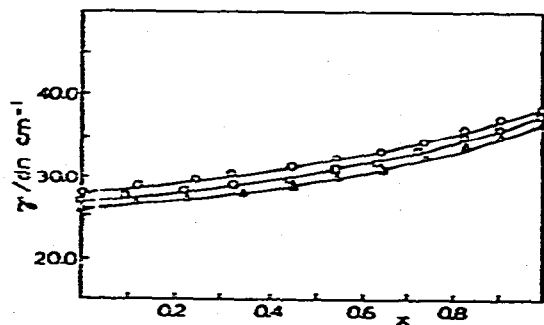


Fig. 3. Plot of surface tension  $\gamma$  against mole fraction  $x$  for the system  $x$  1,2-dibromoethane +  $(1-x)$  toluene at 298.15, 303.15 and 308.15 K.  $\circ$ — $\circ$ , 298.15 K;  $\square$ — $\square$ , 303.15 K;  $\triangle$ — $\triangle$ , 308.15 K.

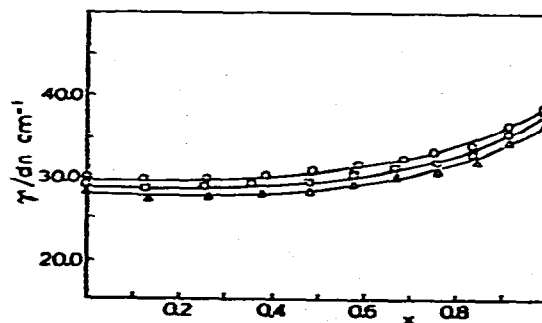


Fig. 4. Plot of surface tension  $\gamma$  against mole fraction  $x$  for the system  $x$  1,2-dibromoethane +  $(1-x)$  *o*-xylene at 298.15, 303.15 and 308.15 K.  $\circ$ — $\circ$ , 298.15 K;  $\square$ — $\square$ , 303.15 K;  $\triangle$ — $\triangle$ , 308.15 K.

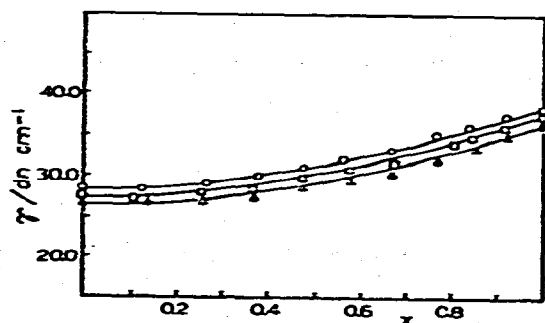


Fig. 5. Plot of surface tension  $\gamma$  against mole fraction  $x$  for the system  $x$  1,2-dibromoethane +  $(1-x)$  *m*-xylene at 298.15, 303.15 and 308.15 K.  $\circ$ — $\circ$ , 298.15 K;  $\square$ — $\square$ , 303.15 K;  $\triangle$ — $\triangle$ , 308.15 K.

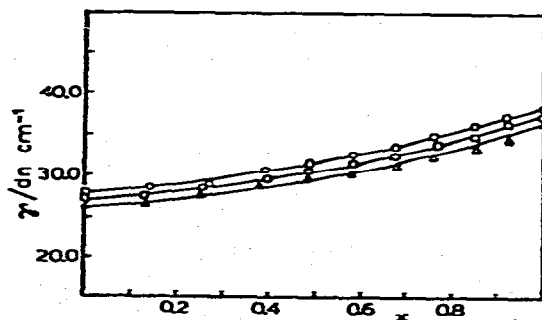


Fig. 6. Plot of surface tension  $\gamma$  against mole fraction  $x$  for the system  $x$  1,2-dibromoethane +  $(1-x)$  *p*-xylene at 298.15, 303.15 and 308.15 K.  $\circ$ — $\circ$ , 298.15 K;  $\square$ — $\square$ , 303.15 K;  $\triangle$ — $\triangle$ , 308.15 K.

length and weight of mercury thread in its different parts. The diameter of the capillary was found to be reproducible to  $\pm 0.001$  cm. The glass cell containing the mixture and capillaries was placed in a water-filled thermostat. The angle of contact of the liquid and glass was taken to be zero. Densities of the mixtures were taken from excess volume measurements<sup>12</sup>. Furthermore two capillaries of different diameter were always employed so as to reduce errors in the measurement of lower meniscus of the liquid in the capillary. The difference  $\Delta h$  in the heights of the liquid in two capillaries was noted and the surface tension was determined from the relation

$$\gamma = 0.5 \Delta h d g r_1 r_2 / (r_1 - r_2) \quad (1)$$

where  $r_1$  and  $r_2$  are the radii of the capillaries. The surface tension agree to within  $0.1 \text{ dn cm}^{-1}$  with their corresponding literature values<sup>13,14</sup>.

## RESULTS

Surface tensions of the mixtures of 1,2-dibromoethane + cyclohexane, + benzene, + toluene, + *o*-xylene, + *m*-xylene, and + *p*-xylene were determined from relation (1) at 298.15, 303.15, and 308.15 K as a function of composition. The surface tension values are plotted in Figs. 1-6.

## DISCUSSION

Eotvos found that molar surface energy  $\gamma(M/d)^{2/3}$  is a linear function of temperature, which can be expressed by the relation:

$$-\frac{\partial}{\partial T} [\gamma(M/d)^{2/3}] = k \quad (2)$$

where  $\gamma$  is the surface tension,  $M$  the molecular weight,  $d$  the density of the liquid and  $k$  the Eotvos Universal constant (for normal non-associating liquids:  $k = 2.12$ ). By integrating eqn (2) we get

$$-[\gamma_2(M/d_2)^{2/3} - \gamma_1(M/d_1)^{2/3}] = k(T_2 - T_1) \quad (3)$$

The values of  $k$  for the pure components and equimolar mixtures were calculated from eqn (3) and are recorded in Table 1.

The values of  $k$  for all these equimolar mixtures deviate to a great extent from 2.12, indicating that these mixtures are somewhat associated in nature.

The average potential model assumes that the exact interactions between the molecules can be replaced in the configurational partition function of the solution by average interactions which depend in the case of random mixing on the individual interactions and on composition. Assuming the validity of mean interactions in the surface phase and surface phase to be monomolecular, Prigogine and Englert-Chwoles deduced the expression for the surface tension. The expression in terms of

TABLE 1

EOTVOS CONSTANTS OF PURE COMPONENTS AND EQUIMOLAR MIXTURES  
(in the range 298.15–303.15 K)

System	$(M/d)^{\frac{2}{3}}$		$k$
	298.15 K	303.15 K	
1,2-Dibromoethane	19.591	19.723	1.94
cyclohexane	22.750	22.942	2.12
benzene	19.991	20.171	2.05
toluene	22.524	22.710	2.07
<i>o</i> -xylene	24.474	24.632	2.02
<i>m</i> -xylene	24.770	24.924	2.03
<i>p</i> -xylene	24.854	25.022	1.99
1,2-Dibromoethane +			
cyclohexane	21.171	21.333	3.24
+ benzene	19.791	19.947	3.49
+ toluene	21.057	21.217	3.95
+ <i>o</i> -xylene	22.033	22.178	3.55
+ <i>m</i> -xylene	22.181	22.324	4.24
+ <i>p</i> -xylene	22.223	22.373	3.78

the parameters  $\delta$ ,  $\theta$  and  $\rho$  is given below:

$$\begin{aligned} \frac{\gamma^E}{x(1-x)} = & \gamma_{AA} \left( \frac{23}{2} \rho^2 - \rho \delta \right) + (\gamma_{AA} - T \gamma'_{AA}) [2\theta - 18\rho^2 - 40\rho(1-x) + 2\rho\delta] + \\ & + \frac{1}{2} T^2 \gamma'_{AA} [-\delta^2 + 4\theta\delta(1-x) + 4\theta^2 x(1-x)] - \\ & - \frac{1}{2} [(\gamma_{AA} - T \gamma'_{AA}) \{-\delta + 2\theta(1-x) - 2\theta x\} + 2\rho \gamma_{AA}]^2 a/kT \end{aligned} \quad (4)$$

where  $\delta$ ,  $\theta$  and  $\rho$  are given by

$$\theta = (\epsilon_{AB}^* - \epsilon_{AA/2}^* - \epsilon_{BB/2}^*) / \epsilon_{AA}^*; \quad \delta = (\epsilon_{BB}^* / \epsilon_{AA}^*) - 1; \quad \rho = (r_{BB}^* / r_{AA}^*) - 1 \quad (5)$$

where  $\epsilon_{ij}^*$  and  $r_{ij}^*$  are the scale factors for intermolecular interaction energy given by  $\epsilon(r) = \epsilon^* \phi(r/r^*)$ , which depend on the pairs AA, BB and AB;  $a$  is the molecular surface area, and  $k$ , the Boltzman constant.

In our calculations from this theory, a deviations from the combining rule was made, i.e., eqn (4) was simplified for dispersion forces, i.e.,  $\theta = \delta^2/\delta$ . The second component was taken as reference in each cases and  $\gamma^E$  values were computed. The values of  $\gamma_{mix}$  in place of  $\gamma^E$  are recorded in Table 2.

Bellemans and Stecki have suggested that there is no need to specify any layer in which composition differs from that of the bulk phase and so surface tension was calculated by applying the expansion method of Krikwood<sup>15</sup> upto second order terms. The final expression for surface tension was given by

$$\frac{\gamma^E}{x(1-x)} = -Zwm - \frac{1}{2kT} [(\gamma_{BB} - \gamma_{AA})a + Zmw(x_B - x_A)^2] + \frac{Zw^2 m}{kT} x_A x_B + \dots \quad (6)$$

where  $a$  is the area occupied by one molecule on the surface phase and is given by

$$a = \frac{1}{2}(M_A/Nd_A)^{2/3} + \frac{1}{2}(M_B/Nd_B)^{2/3} \quad (7)$$

where  $M_A$  and  $M_B$  are molecular weights,  $d$ , the density,  $N$ , the Avogadro number.  $Z$  and  $Z(1-m)$  are respectively the number of first neighbours of a molecule in the bulk phase and on the surface (in our case  $Z=6$ ,  $m=\frac{1}{2}$ ).  $\gamma^E$  values for mixtures were computed from eqn (6) and  $\gamma_{\text{mix}}$  as a function of composition are recorded in Table 2.

TABLE 2

CALCULATED AND EXPERIMENTAL VALUES OF  $\gamma_{\text{mix}}$  AT DIFFERENT COMPOSITIONS OF MIXTURES

$x$	$\gamma_{\text{mix}} (dn \text{ cm}^{-1})$				$x$	$\gamma_{\text{mix}} (dn \text{ cm}^{-1})$			
	<i>Expt.</i>	<i>Englert-Chwoles</i>	<i>Belle-mans</i>	<i>Hilde-brand</i>		<i>Expt.</i>	<i>Englert-Chwoles</i>	<i>Belle-mans</i>	<i>Hilde-brand</i>
<i>x</i> 1,2-Dibromoethane + cyclohexane (1-x) at 298.15 K									
0.1	25.2	25.3	25.3	25.4	0.2	25.9	25.9	26.0	26.1
0.3	26.7	26.8	26.8	26.9	0.4	28.0	28.1	28.2	28.2
0.5	29.5	29.7	29.8	29.8	0.6	31.0	31.2	31.2	31.3
0.7	32.8	32.9	33.0	33.0	0.8	34.4	34.5	34.6	34.6
0.9	36.3	36.4	36.5						
<i>x</i> 1,2-Dibromoethane + (1-x) cyclohexane at 303.15 K									
0.1	24.2	24.3	24.4	24.4	0.2	24.8	24.9	24.9	25.0
0.3	25.6	25.7	25.8	25.9	0.4	26.8	26.9	26.9	27.0
0.5	28.2	28.4	28.4	28.5	0.6	29.9	30.1	30.1	30.2
0.7	31.7	31.8	31.9	31.9	0.8	33.4	33.5	33.6	33.6
0.9	35.3	35.4	35.5	35.5					
<i>x</i> 1,2-Dibromoethane + (1-x) cyclohexane at 308.15 K									
0.1	23.2	23.3	23.4	23.4	0.2	23.8	23.9	24.0	24.1
0.3	24.5	24.6	24.7	24.7	0.4	25.6	25.8	25.8	25.9
0.5	27.0	27.3	27.3	27.4	0.6	28.6	28.8	28.8	28.9
0.7	30.5	30.7	30.7	30.8	0.8	32.3	32.4	32.4	32.5
0.9	34.3	34.3	34.5	34.5					
<i>x</i> 1,2-Dibromoethane + (1-x) benzene at 298.15 K									
0.1	28.4	28.6	28.7	28.8	0.2	28.9	29.1	29.2	29.2
0.3	29.7	29.9	29.9	30.0	0.4	30.5	30.7	30.8	30.9
0.5	31.5	31.8	31.9	31.9	0.6	32.4	32.6	32.6	32.7
0.7	33.8	34.0	34.1	34.1	0.8	35.0	35.1	35.2	35.2
0.9	36.6	36.7	36.8	36.9					
<i>x</i> 1,2-Dibromoethane + (1-x) benzene at 303.15 K									
0.1	27.5	27.7	27.8	27.8	0.2	28.0	28.2	28.3	28.3
0.3	28.7	28.9	28.9	29.0	0.4	29.5	29.7	29.8	29.8
0.5	30.4	30.6	30.7	30.7	0.6	31.4	31.6	31.6	31.7
0.7	32.8	33.0	33.1	33.2	0.8	34.0	33.1	34.2	34.2
0.9	35.6	35.7	35.8	35.9					

(Table continued on p. 190)

TABLE 2 (continued)

<i>x</i>	$\gamma_{\text{mix}} \text{ (dn cm}^{-1}\text{)}$				<i>x</i>	$\gamma_{\text{mix}} \text{ (dn cm}^{-1}\text{)}$			
	<i>Expt.</i>	<i>Englert-Churoles</i>	<i>Belle-mans</i>	<i>Hilde-brand</i>		<i>Expt.</i>	<i>Englert-Churoles</i>	<i>Belle-mans</i>	<i>Hilde-brand</i>
<i>x</i> 1,2-Dibromoethane + (1 - <i>x</i> ) benzene at 308.15 K									
0.1	26.6	26.8	26.8	26.9	0.2	27.0	27.2	27.3	27.3
0.3	27.7	27.9	27.9	27.9	0.4	28.4	28.6	28.7	28.8
0.5	29.3	29.5	29.5	29.6	0.6	30.3	30.5	30.6	30.7
0.7	31.8	31.9	32.0	32.0	0.8	33.1	33.2	33.2	33.3
0.9	34.8	34.9	34.9	35.0					
<i>x</i> 1,2-Dibromoethane + (1 - <i>x</i> ) toluene at 298.15 K									
0.1	28.5	28.7	28.8	28.9	0.2	29.2	29.4	29.5	29.6
0.3	30.0	30.2	30.3	30.4	0.4	30.9	31.1	31.2	31.3
0.5	31.8	32.2	32.2	32.2	0.6	32.7	32.9	32.9	33.1
0.7	34.0	33.3	34.4	34.5	0.8	35.3	35.5	35.6	35.7
0.9	36.8	37.0	37.1	37.1					
<i>x</i> 1,2-Dibromoethane + (1 - <i>x</i> ) toluene at 303.15 K									
0.1	27.7	27.9	28.0	28.1	0.2	28.4	28.6	28.6	28.7
0.3	29.0	29.2	29.3	29.3	0.4	29.8	30.1	30.1	30.2
0.5	30.7	31.0	31.1	31.1	0.6	31.6	31.9	31.9	32.0
0.7	34.0	34.3	34.4	34.5	0.8	35.3	35.5	35.6	35.7
0.9	36.8	37.0	37.1	37.1					
<i>x</i> 1,2-Dibromoethane + (1 - <i>x</i> ) toluene at 308.15 K									
0.1	26.9	27.1	27.3	27.3	0.2	27.5	27.7	27.8	27.8
0.3	28.1	28.3	28.4	28.4	0.4	28.8	28.9	28.9	29.1
0.5	29.6	30.0	30.0	30.1	0.6	30.6	30.8	31.0	31.1
0.7	32.0	32.3	32.4	32.4	0.8	33.5	33.7	33.8	33.8
0.9	35.1	35.2	35.3	35.3					
<i>x</i> 1,2-Dibromoethane + (1 - <i>x</i> ) <i>o</i> -xylene at 298.15 K									
0.1	29.6	29.8	29.9	30.0	0.1	29.8	30.0	30.0	30.1
0.3	30.0	30.2	30.3	30.4	0.4	30.3	30.6	30.6	30.7
0.5	30.7	31.1	31.1	31.2	0.6	31.4	31.6	31.7	31.8
0.7	32.3	32.5	32.6	32.6	0.8	33.8	34.0	34.1	34.1
0.9	35.7	35.9	35.9	36.0					
<i>x</i> 1,2-Dibromoethane + (1 - <i>x</i> ) <i>o</i> -xylene at 303.15 K									
0.1	28.6	28.8	28.9	28.9	0.2	28.7	28.9	29.0	29.1
0.3	28.9	29.1	29.2	29.3	0.4	29.2	29.5	29.5	29.6
0.5	29.5	29.8	29.8	29.9	0.6	30.3	30.6	30.6	30.7
0.7	31.2	31.5	31.5	31.6					
0.9	34.7	34.9	34.8	35.0					
<i>x</i> 1,2-Dibromoethane + (1 - <i>x</i> ) <i>o</i> -xylene at 308.15 K									
0.1	27.6	27.8	27.9	27.9	0.2	27.7	27.9	28.0	28.1
0.3	27.8	28.0	28.1	28.2	0.4	28.0	28.3	28.4	28.4
0.5	28.3	28.6	28.7	28.8	0.6	29.1	29.4	29.4	29.5
0.7	30.1	30.4	30.4	30.5	0.8	31.7	31.9	32.0	32.0
0.9	33.7	33.9	34.0	34.0					

TABLE 2 (continued)

<i>x</i>	$\gamma_{mix}$ (dn cm <sup>-1</sup> )				<i>x</i>	$\gamma_{mix}$ (dn cm <sup>-1</sup> )			
	<i>Expt.</i>	<i>Englert-Chwoles</i>	<i>Belle-mans</i>	<i>Hildebrand</i>		<i>Expt.</i>	<i>Englert-Chwoles</i>	<i>Belle-mans</i>	<i>Hildebrand</i>
<i>x</i> 1,2-Dibromoethane + (1- <i>x</i> ) <i>m</i> -xylene at 298.15 K									
0.1	28.5	28.7	29.8	28.9	0.2	28.8	29.0	29.1	29.1
0.3	29.3	29.5	29.5	29.6	0.4	30.1	30.4	30.4	30.5
0.5	31.3	31.4	31.5	31.6	0.6	32.2	32.5	32.6	32.6
0.7	33.5	33.8	33.9	33.9	0.8	35.1	35.3	35.4	35.5
0.9	36.7	36.9	37.0	37.0					
<i>x</i> 1,2-Dibromoethane + (1- <i>x</i> ) <i>m</i> -xylene at 303.15 K									
0.1	27.6	27.8	27.9	27.9	0.2	27.8	28.0	28.1	28.1
0.3	28.2	28.5	28.5	28.6	0.4	28.9	29.2	29.3	29.4
0.5	29.8	30.1	30.2	30.2	0.6	31.0	31.3	31.3	31.4
0.7	32.4	32.6	32.7	32.7	0.8	34.0	34.2	34.3	34.3
0.9	35.7	35.9	36.0	36.0					
<i>x</i> 1,2-Dibromoethane + (1- <i>x</i> ) <i>m</i> -xylene at 308.15 K									
0.1	26.7	26.9	27.0	27.1	0.2	26.8	37.0	27.1	27.1
0.3	27.1	27.3	27.4	27.4	0.4	27.7	28.0	28.1	28.2
0.5	28.6	28.9	29.0	29.1	0.6	28.8	30.1	30.1	30.2
0.7	31.3	31.6	31.6	31.7	0.8	33.0	32.2	33.3	33.3
0.9	34.7	34.9	35.0	35.0					
<i>x</i> 1,2-Dibromoethane + (1- <i>x</i> ) <i>p</i> -xylene at 298.15 K									
0.1	28.5	28.7	28.8	28.8	0.2	29.2	29.4	29.5	29.5
0.3	30.1	30.3	30.4	30.5	0.4	30.9	31.2	31.3	31.4
0.5	31.8	32.1	32.2	32.3	0.6	32.8	33.1	33.3	33.3
0.7	34.0	34.3	34.4	34.4	0.8	35.4	35.6	35.6	35.7
0.9	36.9	37.1	37.2	37.2					
<i>x</i> 1,2-Dibromoethane + (1- <i>x</i> ) <i>p</i> -xylene at 303.15 K									
0.1	27.7	27.9	27.9	27.9	0.2	28.2	28.4	27.4	28.5
0.3	29.0	29.2	29.2	29.3	0.4	29.8	30.1	30.1	30.2
0.5	30.6	30.8	30.9	30.9	0.6	31.6	31.6	31.9	31.9
0.7	32.9	33.1	33.1	33.2	0.8	34.4	34.5	34.6	34.6
0.9	36.0	36.1	36.2	36.2					
<i>x</i> 1,2-Dibromoethane + (1- <i>x</i> ) <i>p</i> -xylene at 308.15 K									
0.1	26.8	26.9	26.9	27.0	0.2	27.3	27.4	27.4	27.5
0.3	28.0	28.2	28.3	28.3	0.4	28.7	28.9	28.9	29.0
0.5	29.5	29.7	29.8	29.9	0.6	30.6	30.8	30.8	30.9
0.7	31.9	32.1	32.2	32.3	0.8	33.4	33.5	33.5	33.6
0.9	35.1	35.2	35.2	35.3					

Hildebrand's ideal solution model assumes both the liquid and surface layer form ideal solutions and the equation for  $\gamma_{mix}$  is given by

$$\gamma_{mix} = x\gamma_{AA} + (1-x)\gamma_{BB} - \frac{A}{2RT} (\gamma_{AA} - \gamma_{BB})^2 x(1-x) \quad (8)$$

where  $A$  is the surface occupancy of the molecules ( $\text{cm}^2 \text{mol}^{-1}$ ). While computing  $\gamma_{\text{mix}}$  from this expression,  $A = (A_1 + A_2)/2$  was assumed.  $\gamma_{\text{mix}}$  values computed from this approach are recorded in Table 2. The values of  $\gamma_{\text{mix}}$  obtained on the basis of the approaches of Englert-Chwoles are in better agreement with the corresponding experimental values as obtained on the basis of the theories of Bellemans-Stecki and Hildebrand.

Quantitative treatment of the dependence of surface tension of binary mixtures on their composition have been carried by Belton and Evans, Schuchowitky and Guggenheim. Using quasi-crystalline model, Guggenheim<sup>4</sup> developed a statistical treatment of surface tension of binary regular solution. The final equations due to him are:

$$\exp(-\gamma a/kT) = x_A \exp(-\gamma_A a/kT) \exp(mwx_A^2/kT) + x_B \exp(-\gamma_B a/kT) \exp(mwx_B^2/kT) \quad (9)$$

where  $w$  is the interchange energy,  $x_A$  and  $x_B$  are the mole fractions,  $\gamma_A$  and  $\gamma_B$  are the surface tensions of pure liquids,  $\gamma$  is the surface tension of the mixture. Interchange energies of the equimolar mixtures were computed from eqn (9) and are recorded in Table 3.

TABLE 3  
INTERCHANGE ENERGIES OF MIXTURES

System	Average surface area/ $A^{\circ 2}$			$w/K$ ( $\text{J mol}^{-1}$ )		
	298.15 K	303.15 K	308.15 K	298.15 K	303.15 K	303.13 K
1,2-Dibromoethane + cyclohexane	29.69	29.80	39.91	1.20	1.41	1.61
+ benzene	27.75	27.85	27.96	0.62	0.72	0.92
+ toluene	29.51	29.63	29.75	0.52	0.85	0.94
+ <i>o</i> -xylene	30.91	31.00	31.10	1.19	1.33	1.70
+ <i>m</i> -xylene	31.09	31.19	31.30	0.96	1.13	1.55
+ <i>p</i> -xylene	31.16	31.24	31.37	0.59	0.87	0.99

The interchange energies for all these systems are positive but small in magnitude, indicating that these mixtures showed a tendency of association.

It would now be interesting to examine the conclusions obtained from the computation of surface heat of mixing from surface tension data. The surface heat of mixing per unit area could be written by the relation

$$\Delta H^s/A = H^s/A - [x_1(H^s/A)_1 + x_2(H^s/A)_2] \quad (10)$$

where  $(H^s/A)_1$  is the surface heat content of the pure component  $A$  and  $H^s/A$  is the surface heat content of the mixture. The change in the value of surface tension is given by

$$\Delta\gamma = H^s/A - T\Delta S^s/A$$



$$\text{and } S^s/A = -d\gamma/dT \quad \text{and} \quad H^s/A = \gamma - Td\gamma/dT \quad (11)$$

The values of  $S^s/A$ ,  $H^s/A$  and  $\Delta H^s/A$  were computed for these mixtures over the whole composition range at 298.15 K and are recorded in Tables 4 and 5.  $\Delta H^s/A$  values are plotted against composition at 298.15 K for all these mixtures in Figs 7-12.

TABLE 4

AVERAGE AREA PER MOLECULE, SURFACE ENTROPY AND SURFACE HEATS OF PURE COMPONENTS

System	Average area/A <sup>2</sup>			S <sup>s</sup> /A (erg deg <sup>-1</sup> cm <sup>-2</sup> )	H <sup>s</sup> /A (erg cm <sup>-2</sup> )
	298.15 K	303.15 K	308.15 K		
1,2-Dibromoethane	27.47	27.55	27.65	0.124	75.07
cyclohexane	31.91	32.04	32.17	0.133	64.54
benzene	28.03	28.16	28.27	0.137	68.51
toluene	31.55	31.71	31.84	0.114	61.99
<i>o</i> -xylene	34.34	34.44	34.55	0.121	65.74
<i>m</i> -xylene	34.72	34.83	34.95	0.109	60.87
<i>p</i> -xylene	34.85	34.93	35.09	0.135	68.14

TABLE 5

SURFACE ENTROPY AND SURFACE HEATS OF MIXING OF MIXTURES AT 298.15 K

<i>x</i>	S <sup>s</sup> /A (erg deg <sup>-1</sup> cm <sup>-2</sup> )	H <sup>s</sup> /A (erg cm <sup>-2</sup> )	ΔH <sup>s</sup> /A (erg cm <sup>-2</sup> )	<i>x</i>	S <sup>s</sup> /A (erg deg <sup>-1</sup> cm <sup>-2</sup> )	H <sup>s</sup> /A (erg cm <sup>-2</sup> )	ΔH <sup>s</sup> /A (erg cm <sup>-2</sup> )
<i>x</i> 1,2-Dibromoethane + (1- <i>x</i> ) cyclohexane							
0.1	0.200	84.83	19.24	0.2	0.210	88.51	21.86
0.3	0.220	92.29	24.59	0.4	0.240	99.56	30.81
0.5	0.250	104.04	34.24	0.6	0.240	102.56	31.70
0.7	0.230	101.37	29.46	0.8	0.215	98.50	25.54
0.9	0.200	95.93	21.91				
<i>x</i> 1,2-Dibromoethane + (1- <i>x</i> ) benzene							
0.1	0.180	82.07	12.90	0.2	0.190	85.60	15.78
0.3	0.200	89.33	18.85	0.4	0.210	93.11	21.98
0.5	0.220	97.09	25.30	0.6	0.215	96.50	24.05
0.7	0.200	93.43	20.33	0.8	0.190	91.65	17.89
0.9	0.180	90.27	15.86				
<i>x</i> 1,2-Dibromoethane + (1- <i>x</i> ) toluene							
0.1	0.160	76.20	12.90	0.2	0.170	79.80	15.28
0.3	0.190	86.65	20.74	0.4	0.210	93.51	26.29
0.5	0.221	97.69	29.16	0.6	0.210	95.31	25.47
0.7	0.200	93.65	22.48	0.8	0.180	88.97	16.52
0.9	0.170	87.49	13.73				

(Table continued on p. 194)

TABLE 5 (continued)

$x$	$S^s/A$ ( $\text{erg deg}^{-1} \text{cm}^{-2}$ )	$H^s/A$ ( $\text{erg cm}^{-2}$ )	$\Delta H^s/A$ ( $\text{erg cm}^{-2}$ )	$x$	$S^s/A$ ( $\text{erg deg}^{-1} \text{cm}^{-2}$ )	$H^s/A$ ( $\text{erg cm}^{-2}$ )	$\Delta H^s/A$ ( $\text{erg cm}^{-2}$ )
<i>x</i> 1,2-Dibromoethane + (1- <i>x</i> ) <i>o</i> -xylene							
0.1	0.200	89.23	22.56	0.2	0.210	92.41	22.56
0.3	0.220	95.59	27.05	0.4	0.230	98.87	29.40
0.5	0.240	102.26	31.86	0.6	0.235	101.47	30.13
0.7	0.220	97.89	25.62	0.8	0.210	96.41	23.21
0.9	0.200	95.33	21.19				
<i>x</i> 1,2-Dibromoethane + (1- <i>x</i> ) <i>m</i> -xylene							
0.1	0.180	82.17	19.88	0.2	0.200	88.43	24.72
0.3	0.220	94.89	29.76	0.4	0.240	101.66	35.11
0.5	0.250	105.64	37.67	0.6	0.240	103.76	34.37
0.7	0.220	99.69	28.28	0.8	0.210	97.71	25.48
0.9	0.200	96.33	22.68				
<i>x</i> 1,2-Dibromoethane + (1- <i>x</i> ) <i>p</i> -xylene							
0.1	0.170	79.19	10.36	0.2	0.190	85.85	16.32
0.3	0.210	92.66	22.40	0.4	0.225	97.98	27.07
0.5	0.235	101.87	30.27	0.6	0.225	99.88	27.58
0.7	0.210	96.61	23.61	0.8	0.200	95.03	21.35
0.9	0.180	90.57	16.19				

From Table 5 it is evident that  $\Delta H^s/A$  values are positive over the whole composition range suggesting the presence of dispersion forces in these mixtures. The plots of  $\Delta H^s/A$  against composition are symmetrical and agree in shape with the plots of other excess thermodynamic functions, i.e.,  $V^E$ ,  $G^E$  and  $H^E$  for majority of the mixtures.

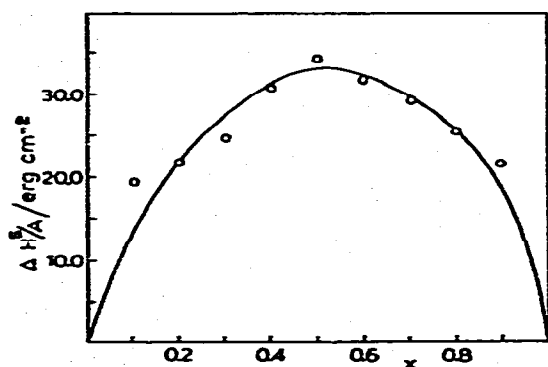


Fig. 7. Plot of surface heat of mixing  $\Delta H^s/A$  against mole fraction  $x$  for the system 1,2-dibromoethane + (1- $x$ ) cyclohexane at 298.15 K.

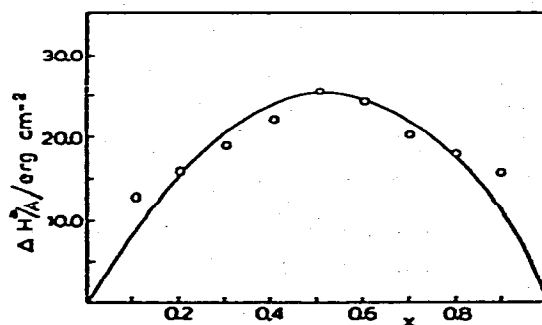


Fig. 8. Plot of surface heat of mixing  $\Delta H^s/A$  against mole fraction  $x$  for the system  $x$  1,2-dibromoethane + (1- $x$ ) benzene at 298.15 K.

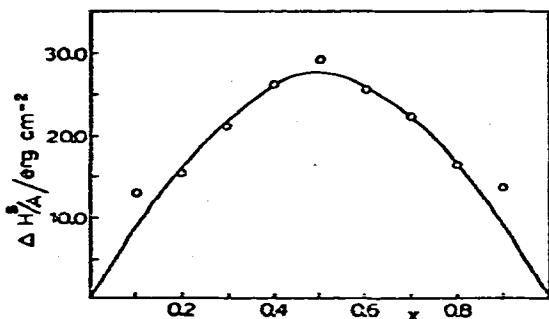


Fig. 9. Plot of surface heat of mixing  $\Delta H_s^2/A$  against mole fraction  $x$  for the system 1,2-dibromoethane +  $(1-x)$  toluene at 298.15 K.

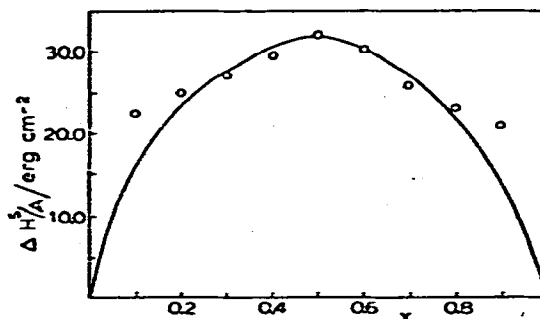


Fig. 10. Plot of surface heat of mixing  $\Delta H_s^2/A$  against mole fraction  $x$  for the system 1,2-dibromoethane +  $(1-x)$  *o*-xylene at 298.15 K.

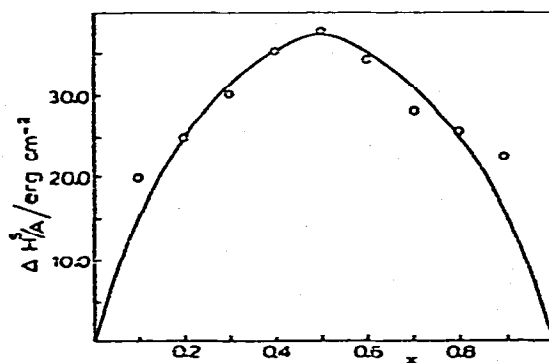


Fig. 11. Plot of surface heat of mixing  $\Delta H_s^2/A$  against mole fraction  $x$  for the system  $x$  1,2-dibromoethane +  $(1-x)$  *m*-xylene at 298.15 K.

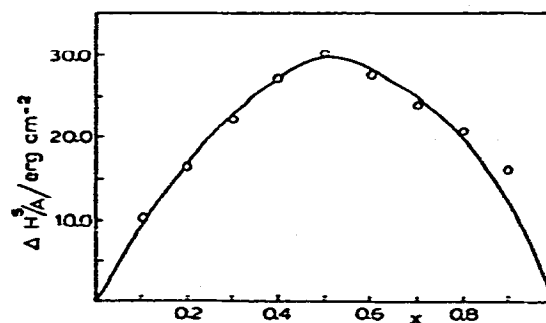


Fig. 12. Plot of surface heat of mixing  $\Delta H_s^2/A$  against mole fraction  $x$  for the system  $x$  1,2-dibromoethane +  $(1-x)$  *p*-xylene at 298.15 K.

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