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# EXCESS VOLUMES OF MIXING OF 1,2-DICHLOROETHANE AND AROMATIC HYDROCARBONS

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## ABSTRACT

Excess volumes of mixing, $V^E$, for binary mixtures of 1,2-dichloroethane with benzene, toluene, *o*-, *m*-, and *p*-xylenes have been determined at 308.15 K over the complete composition range. $V^E$ is positive for all these mixtures and varies in the order *m*-xylene > *o*-xylene > *p*-xylene > benzene > toluene. The experimental data have been analyzed in terms of the Prigogine's average potential cell model coupled with Balescu's theory. The calculated $V^E$ values do not agree with the corresponding experimental values.

## INTRODUCTION

1,2-Dichloroethane exists as *trans* and *gauche* conformational isomers and the equilibrium between these isomers depends on the stabilization of the *gauche* form by either a medium of high dielectric constant or by a polarizable surrounding. Wilhelm et al. [1], from their heat capacity measurements on 1,2-dichloroethane + benzene systems, have inferred that the rotation of both the components of these mixtures is hindered. However, aromatic hydrocarbons are potential electron donors and their mixtures with such simple compounds as carbon tetrachloride have been interpreted [2], in terms of charge-transfer interactions between the $\pi$ electrons of the aromatic ring and the empty 3*d* levels of halogens in carbon tetrachloride. It would thus be interesting to know as to how far this conclusion is true in the interaction of these aromatic hydrocarbons with 1,2-dichloroethane which has a permanent dipole moment of 2.94 D [3].

## EXPERIMENTAL

Analytical grade (BDH) benzene, toluene, *o*-, *m*- and *p*-xylene were purified as described earlier [4]. 1,2-Dichloroethane was purified as described elsewhere [5]. The purity of the final samples was checked by density determinations at 298.15 ± 0.01 K (293.15 ± 0.01 K in the case of *m*-xylene) which agreed to within ±0.00005 g/ml with the corresponding literature values [6—9].

The excess volumes of mixing as a function of composition were measured dilatometrically as described earlier [10]. The temperature of the water bath was controlled to ± 0.01 K

## RESULTS

The molar excess volumes of mixing, $V^E$, data for 1,2-dichloroethane + benzene, toluene, *o*-, *m*- and *p*-xylenes at 308.15 K are recorded in Table 1 The $V^E$ data were fitted to the equation

$$V^E/x_1(1-x_1) = V_0 + V_1(2x_1-1) + V_2(2x_1-1)^2 \tag{1}$$

TABLE 1

Experimentally measured excess volumes of mixing $V^E$ for 1,2-dichloroethane (1) + aromatic hydrocarbon (2) mixtuees at 308.15 K

| Mole fraction of (1) | $V^E$ (cm$^3$ mole$^{-1}$) | Mole fraction of (1) | $V^E$ (cm$^3$ mole$^{-1}$) |
|---|---|---|---|
| *1,2-Dichloroethane (1) + benzene (2)* | | *1,2-Dichloroethane (1) + o-xylene (2)* | |
| 0.1523 | 0.123 | 0.0692 | 0.062 |
| 0.3491 | 0.206 | 0.1608 | 0.132 |
| 0.4195 | 0.215 | 0.2339 | 0.182 |
| 0.5242 | 0.219 | 0.3564 | 0.245 |
| 0.6189 | 0.199 | 0.4316 | 0.285 |
| 0.6913 | 0.181 | 0.5202 | 0.311 |
| 0.7816 | 0.148 | 0.5606 | 0.317 |
| 0.8879 | 0.079 | 0.7608 | 0.261 |
| | | 0.8395 | 0.197 |
| *1,2-Dichloroethane (1) + toluene (2)* | | 0.8975 | 0.138 |
| 0.0785 | 0.036 | 0.9482 | 0.075 |
| 0.1481 | 0.066 | | |
| 0.2148 | 0.093 | *1,2-Dichloroethane (1) + p-xylene (2)* | |
| 0.3474 | 0.139 | 0.1354 | 0.098 |
| 0.4616 | 0.173 | 0.2956 | 0.195 |
| 0.5709 | 0.180 | 0.4503 | 0.055 |
| 0.7309 | 0.154 | 0.5123 | 0.273 |
| 0.7801 | 0.135 | 0.6556 | 0.271 |
| 0.8281 | 0.116 | 0.7221 | 0.251 |
| 0.8679 | 0.096 | 0.7946 | 0.218 |
| 0.9007 | 0.078 | 0.8532 | 0.175 |
| 0.9674 | 0.026 | 0.9330 | 0.089 |
| *1,2-Dichloroethane (1) + m-xylene (2)* | | | |
| 0.0571 | 0.043 | | |
| 0.1425 | 0.111 | | |
| 0.2917 | 0.241 | | |
| 0.4814 | 0.350 | | |
| 0.5695 | 0.372 | | |
| 0.6684 | 0.359 | | |
| 0.7492 | 0.319 | | |
| 0.8369 | 0.241 | | |
| 0.8879 | 0.184 | | |
| 0.9629 | 0.066 | | |

TABLE 2

Paramaters of eqn (1) along with the standard deviations $\sigma(V^E)$ in cm$^3$ mole$^{-1}$, for 1,2-dichloroethane (1) + aromatic hydrocarbon (2) at 308.15 K

| System | $V_0$ | $V_1$ | $V_2$ | $\sigma(V^E)$ |
|---|---|---|---|---|
| Benzene + 1,2-dichloroethane | 0.8714 | −0.0913 | 0.0332 | 0.003 |
| Toluene + 1,2-dichloroethane | 0.6942 | 0.2141 | −0.0431 | 0.002 |
| *o*-Xylene + 1,2-dichloroethane | 1.2174 | 0.3464 | 0.0250 | 0.004 |
| *m*-Xylene + 1,2-dichloroethane | 1.4289 | 0.6056 | −0.1544 | 0.002 |
| *p*-Xylene + 1,2-dichloroethane | 1.0785 | 0.3839 | 0.0635 | 0.002 |

where $V_0$, $V_1$ and $V_2$ are disposable parameters and $x_1$ is the mole fraction of 1,2-dichloroethane. These parameters have been evaluated by fitting $V^E/x_1(1-x_1)$ to expression (1) by the method of least squares, and are given together with the standard deviation of the molar excess volume of mixing $\sigma(V^E)$ in Table 2

## DISCUSSION

The excess volumes of mixing for 1,2-dichloroethane + aromatic hydrocarbons are positive at all compositions and vary in the order: *m*-xylene > *o*-xylene > *p*-xylene > benzene > toluene. At the simplest qualitative level the excess volume of mixing data can be accounted for if we assume that:

(i) these mixtures are characterized by electron donor—acceptor type interactions in which hydrocarbons behave as electron donors, and

(ii) there is steric repulsion between the components of these binary mixtures

Assuming that the free rotation of 1,2-dichloroethane and benzene in their binary mixture is hindered by electron charge-transfer interactions between them, the introduction of $a$-CH$_3$ substituents in benzene as in toluene, would thus render the $\pi$-cloud of the aromatic ring in toluene to be more labile, so that compared to benzene, toluene should interact strongly with 1,2-dichloroethane. This would mean that $V^E$ for 1,2-dichloroethane + toluene should be small compared to 1,2-dichloroethane + benzene. The experimental data support this conjecture On the other hand, the introduction of 2-CH$_3$ substituents in benzene, as in xylenes, although increasing the $\pi$-electron donating capacity of these compounds, considerably increases the steric repulsion between these bulky CH$_3$ groups and the atoms of 1,2-dichloroethane. From such the $V^E$ value for 1,2-dichloroethane + xylenes would be expected to be more positive than that for 1,2-dichloroethane + benzene or 1,2-dichloroethane + toluene. The experimental data also support this. Again, within the xylenes the steric repulsion for *p*-xylene would be minimum as compared to that for *o*- and *m*-xylenes so that $V^E$ for 1,2-dichloroethane + *p*-xylene should be less positive than that of 1,2-dychloroethane + *o*-xylene or 1,2-dichloroethane + *m*-xylene This has in fact been observed. Such a scheme of interaction would then mean that charge-transfer and steric hindrance are the predominant factors characterizing these mixtures.

The presence of a permanent dipole in 1,2-dichloroethane would contribute to the potential and hence to the excess volumes of mixing. Consequently it was thought worthwhile to analyze the $V^E$ data for these mixtures in terms of the Prigogine's average potential cell model theory (which takes into account the contribution of central forces to the excess thermodynamic functions) coupled with Balescu's theory (this theory considers dipolar interactions as small perturbations to the interaction due to the central forces). $V^E$ was then expressed as

$$V^E = V_0^E + V_p^E \tag{2}$$

where $V_0^E$ and $V_p^E$ are the contributions to $V^E$ due to the central and dipolar forces, respectively, and were evaluated from the following expressions [11, 12].

$$\begin{aligned}\frac{V_0^E}{x_1x_2} = {} & (\tfrac{3}{2})\, v_1\rho[\theta(x_1 - x_2) + \tfrac{1}{2}\,\delta + \tfrac{11}{4}\,\rho] \\ & + TV_1'[-2\theta + 9\rho^2 + \theta^2 - \tfrac{3}{4}\,\delta^2 + \delta\theta(1 + 2x_2) \\ & - (\tfrac{3}{2})\rho\theta + (\tfrac{9}{4})\rho\delta + (\tfrac{3}{2})\rho\theta(x_1 - x_2) \\ & + \tfrac{1}{2}\, T^2 V_1''[\theta^2 - (\tfrac{3}{4})\delta^2 + \delta\theta(1 + 2x_2)]\end{aligned} \tag{3}$$

$$\begin{aligned}\frac{V_p^E}{x_1x_2} = {} & \Bigl\{-\Gamma_{12}\Bigl[\Bigl(TV_1' + \frac{V_1}{4}\Bigr)(2 + \theta + 3\rho + \\ & + \frac{(x_1 - x_2)}{2}(\delta + 3\rho)) + \tfrac{5}{4}\,\delta(x_2 + \tfrac{1}{2})\Bigr] \\ & + \Gamma_{11}\Bigl[\Bigl(TV_1' + \frac{V_1}{4}\Bigr)(1 + x_1(\theta + \delta/2 + \tfrac{3}{2}\,\rho)) - (\tfrac{5}{8})\delta x_1\Bigr] \\ & + \Gamma_{22}\Bigl[\Bigl(TV_1' + \frac{V_1}{4}\,(1 + 3\rho + (\theta - \delta/2 - (\tfrac{3}{2})\rho)x_2) \\ & + \tfrac{5}{4}\,\delta\Bigl(1 + \frac{x_2}{2}\Bigr)\Bigr]\Bigr\}\end{aligned} \tag{4}$$

The parameters $\delta$, $\rho$, $\Gamma_{ii}$, $\Gamma_{ij}$, in these equations were calculated from the following relations [11,12].

$$(1 + \delta_1) = T_c^2/T_c^1 \tag{5}$$

$$(1 + \rho_1)^3 = P_c^1 T_c^2/P_c^2 T_c^1 \tag{6}$$

$$\Gamma_{ii} = \mu_i^4/\epsilon_{ii}^0 r_{ii}^{06} KT^{1/2} \qquad \Gamma_{ij} = \mu_i^2\mu_j^2/(\epsilon_{ii}\epsilon_{jj})^{1/2}\,(\gamma_{ii}^0 + V_{jj}^0)]^6 KT \tag{7}$$

$$\epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{1/2} \qquad r_{ij} = (r_{ii} + r_{jj})/2(i, j = 1, 2) \tag{8}$$

where the various symbols have their usual meanings [11,12]. The critical constant data and the dipole moments, $\mu$, were taken from the literature [13, 14]. The values of $\epsilon_{22}$ and $r_{22}$ for 1,2-dichloroethane, *o*-, *m*-, *p*-xylenes and toluene were calculated by taking $\epsilon_{11} = r_{11} =$ (the co-ordinate of the mini-

TABLE 3

Comparison of $V^E$ values calculated according to Prigogine and Balescu's theory with the corresponding $V^E$ experimental values at $x_1 = 0.3$, 0.5 and 0.7 at 308 15 K for 1,2-dichloroethane (1) + aromatic hydrocarbons (2)

| System | Mole fraction of 1,2-dichloroethane | | | |
|---|---|---|---|---|
| | 0.3 | 0.5 | 0.7 | $\theta$ |
| Benzene (1) + 1,2-dichloroethane (2) | | | | |
| (1) as ref | −1.023 | 0.217 | 1 39 | 0.613 |
| (2) as ref. | −0.352 | 0.217 | 1.43 | 0.563 |
| Exp. | 0.192 | 0.217 | 0.176 | — |
| Toluene (1) + 1,2-dichloroethane (2) | | | | |
| (1) as ref. | −2 250 | 0.173 | 2.50 | 0.694 |
| (2) as ref. | −2.033 | 0.173 | 2.106 | 0.758 |
| Exp. | 0 129 | 0.173 | 0.165 | — |
| *o*-Xylene (1) + 1,2-dichloroethane (2) | | | | |
| (1) as ref. | −4.030 | 0.304 | 4.50 | 0.858 |
| (2) as ref | −3 984 | 0.304 | 4.50 | 1.195 |
| Exp. | 0 227 | 0.304 | 0 286 | — |
| *m*-Xylene (1) + 1,2-dichloroethane (2) | | | | |
| (1) as ref. | −4.020 | 0.357 | 4.61 | 0.834 |
| (2) as ref. | −3.862 | 0 357 | 4 64 | 1 132 |
| Exp. | 0.244 | 0.357 | 0.346 | — |
| *p*-Xylene (1) + 1,2-dichloroethane (2) | | | | |
| (1) as ref. | −6 554 | 0.269 | 3.373 | 0.899 |
| (2) as ref. | −4.357 | 0 269 | 4.803 | 1 200 |
| Exp | 0.196 | 0 269 | 0.261 | — |

mum in the potential energy curve for benzene from the relations [15]

$$(1 + \delta_1) = \epsilon_{22}/\epsilon_{11} \tag{9}$$

$$(1 + \rho_1)^3 = (r_{22}/r_{11})^3 \tag{10}$$

Evaluation of $V_0^E$ and $V_p^E$ from eqns. (3 and 4) required a knowledge of the value of $\theta$. Since the geometric mean law is obeyed by simple molecules and as there are no independent methods of its evaluation, it was evaluated by fitting $V^E$ data for an equimilar composition to eqn. (2). It was, however, observed that this procedure yielded imaginary values of $\theta$ and to overcome this problem we (as a first approximation) neglected the terms in $\theta^2$ in eqns. (3 and 4) and again evaluated $\theta$ for an equimolar mixture. This value of $\theta$ was next used to evaluate $V^E$ at $x_1 = 0.3$ and 0.7 This procedure was repeated with both components of the mixture taken as references. The calculated $V^E$ values are recorded in Table 3 and they fail (as expected) to describe the general behaviour of $V^E$ with composition

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