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# Solubilities of organoboron compounds in organic solvents. Part 3. Solid–liquid equilibria of some 1,3-diacyloxy-1,3-diethyl-1,3-diboroxanes in heptane or benzene ☆

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## Abstract

The solubilities of two 1,3-diacyloxy-1,3-diethyl-1,3-diboroxanes $[Et(RCOO)B]_2O$ (**A**, R is $CH_3$; **B**; R is $CCl_3$) in heptane and benzene have been determined at temperatures ranging from the melting point of the solute to 273 K. The equilibrium between the two forms of compound **B** has no significant influence on the solubility of this compound. Three correlation methods were applied: the Wilson, UNIQUAC and NRTL models. The average r.m.s. deviations of the solubility temperatures for all measured data was 1.9, 1.6, 2.7 and 2.4 K for the Wilson, Wilson 3, UNIQUAC and NRTL models, respectively.

*Keywords:* Benzene; Heptane; Model; Organoboron compound; SLE; Solubility

## List of symbols

| | |
|---|---|
| $a_{12}$ | binary interaction parameter of the Wilson equation |
| $g_{ij}$ | molar energy of interaction between $i$ and $j$ |
| $\Delta g_{ij} = g_{ij} = g_{ii}$ | difference between energies of interaction |

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☆ For Parts 1 and 2 see Refs. [1,2].

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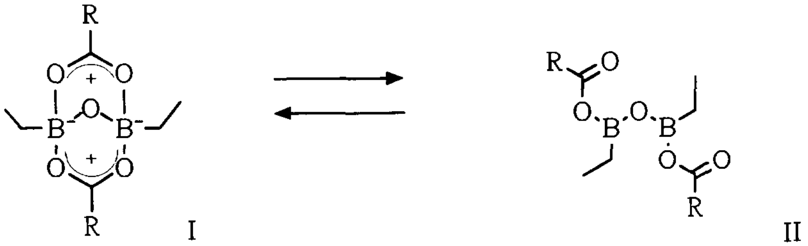
| | |
|---|---|
| $\Delta H_{\mathrm{m1}}$ | molar enthalpy of fusion of the solute |
| $n$ | number of experimental points |
| $l$ | number of adjustable parameters |
| $P_1, P_2$ | adjustable parameters |
| $R$ | universal gas constant |
| $T^{\mathrm{exp}}$ | experimental equilibrium temperature |
| $T^{\mathrm{cal}}$ | calculated equilibrium temperature |
| $T_{\mathrm{m1}}$ | melting point temperature of the pure solute |
| $V_{\mathrm{m}}^{\ominus}$ | molar volume of the solute, solvent |
| $w_i$ | weight of an experimental point |
| $x_1$ | molar fraction of the solute |

*Greek letters*

| | |
|---|---|
| $\gamma_1$ | activity coefficient of the solute |
| $\sigma$ | r.m.s. deviation of temperature |

## 1. Introduction

1,3-Diacyloxy-1,3-diorgano-1,3-diboroxanes $[\mathrm{R'(RCOO)B}]_2\mathrm{O}$ are useful reagents in organic syntheses [3,4]. Chelate-stabilized structure **I** was proposed for some diacyloxydiethyl compounds on the basis of spectroscopic measurements and was recently proved by X-ray diffraction for the substituents R′ is $C_2H_5$ and R is $CH_3$ [5]. The substitution of hydrogen atoms in acyloxy groups by electronegative atoms, e.g. chlorine, decreases the donor ability of the carbonyl oxygen and causes the "open" form **II** to exist in equilibrium with the cyclic one **I** [6]. The aim of this work was to study the solubility of selected compounds of this type in hydrocarbons. Two compounds were chosen for solubility measurements: 1,3-diacetoxy-1,3-diethyl-1,3-diboroxane, $[\mathrm{Et(AcO)B}]_2\mathrm{O}$ (compound **A**), in which only form **I** was found to exist in hydrocarbon solution, and 1,3-diethyl-1,3-bis(trichloroacetoxy)-1,3-diboroxane, $[\mathrm{Et(CCl_3COO)B}]_2\mathrm{O}$ (compound **B**), in which a significant contribution of the form **II** was found in spectroscopic investigations [6].



I

II

Table 1
Characteristics of solutes and solvents

| Compound | $V^{\ominus\,a}/(\mathrm{cm^3\,mol^{-1}})$ | $T_{\mathrm{m1}}/\mathrm{K}$ | $\Delta H_{\mathrm{m1}}/(\mathrm{kJ\,mol^{-1}})$ |
|---|---|---|---|
| $[\mathrm{Et(AcO)B}]_2\mathrm{O}$ (**A**) | 194.39 | 377.15 | 21.60 |
| $[\mathrm{Et(CCl_3COO)B}]_2\mathrm{O}$ (**B**) | 296.11 | 327.15 | 24.22 |
| Benzene | 88.87[b] | | |
| Heptane | 146.49[b] | | |

[a] $V_{\mathrm{m}}^{\ominus}$ is the molar volume at 298.15 K. [b] Data from Ref. [7].

Table 2
Experimental mole fraction solubilities and activity coefficients of compound **A**

| $x_1$ | $T_1/\mathrm{K}$ | $\gamma_1$ | $x_1$ | $T_1/K$ | $\gamma_1$ |
|---|---|---|---|---|---|
| Benzene | | | | | |
| 0.0667 | 281.85 | 1.459 | 0.2497 | 324.35 | 1.305 |
| 0.0805 | 287.35 | 1.443 | 0.2838 | 329.05 | 1.287 |
| 0.1002 | 293.95 | 1.420 | 0.3225 | 333.95 | 1.272 |
| 0.1159 | 298.55 | 1.407 | 0.3442 | 337.15 | 1.283 |
| 0.1405 | 304.55 | 1.378 | 0.4240 | 344.65 | 1.232 |
| 0.1627 | 309.55 | 1.366 | 0.4676 | 347.65 | 1.192 |
| 0.1960 | 315.55 | 1.330 | 0.5090 | 351.05 | 1.177 |
| 0.2234 | 320.45 | 1.323 | 1.0000 | 377.15 | 1.000 |
| Heptane | | | | | |
| 0.0033 | 291.15 | 39.256 | 0.1685 | 348.60 | 3.376 |
| 0.0047 | 297.35 | 33.289 | 0.2799 | 354.00 | 2.277 |
| 0.0066 | 302.15 | 27.534 | 0.3335 | 356.30 | 2.004 |
| 0.0108 | 307.35 | 19.337 | 0.4111 | 358.75 | 1.709 |
| 0.0176 | 315.05 | 14.607 | 0.5034 | 362.05 | 1.490 |
| 0.0284 | 323.35 | 11.201 | 0.6309 | 366.15 | 1.289 |
| 0.0415 | 329.40 | 8.875 | 0.7592 | 370.50 | 1.164 |
| 0.0590 | 334.85 | 7.105 | 0.8374 | 372.85 | 1.103 |
| 0.0838 | 339.95 | 5.618 | 1.0000 | 377.15 | 1.000 |
| 0.1216 | 344.95 | 4.323 | | | |

## 2. Experimental

### 2.1. Materials

1,3-Diacetoxy-1,3-diethyl-1,3-diboroxane (compound **A**) and 1,3-diethyl-1,3-bis(trichloroacetoxy)-1,3-diboroxane (compound **B**) were synthesized as described in Ref. [6] and recrystallized from heptane. The solvents, heptane (VEB Jenapharm, Germany) and benzene (POCh, Poland), were dried over 4A molecular sieves and distilled from benzophenone ketyl through a 50-plate laboratory column. The characteristics of the solutes and solvents are listed in Table 1.

Table 3
Experimental mole fraction solubilities and activity coefficients of compound **B**

| $x_1$ | $T_2$/K | $T_1$/K | $\gamma_1$ | $x_1$ | $T_1$/K | $\gamma_1$ |
|---|---|---|---|---|---|---|
| Benzene | | | | | | |
| 0.0000 | 278.65 | | | 0.2381 | 294.70 | 1.576 |
| 0.0194 | 277.45 | | | 0.2483 | 295.67 | 1.561 |
| 0.0380 | 276.25 | | | 0.2543 | 296.20 | 1.551 |
| 0.0621 | 274.50 | | | 0.2669 | 297.22 | 1.529 |
| 0.0683 | 274.10 | | | 0.2785 | 298.15 | 1.511 |
| 0.0737 | 273.65 | | | 0.2888 | 298.95 | 1.495 |
| 0.0775 | | 273.47 | 2.248 | 0.2998 | 299.80 | 1.481 |
| 0.0829 | | 273.85 | 2.131 | 0.3125 | 300.75 | 1.465 |
| 0.0887 | | 275.05 | 2.088 | 0.3265 | 301.80 | 1.450 |
| 0.0944 | | 276.45 | 2.069 | 0.3416 | 302.97 | 1.439 |
| 0.1013 | | 277.55 | 2.011 | 0.3547 | 303.82 | 1.423 |
| 0.1083 | | 278.70 | 1.964 | 0.3692 | 304.95 | 1.417 |
| 0.1147 | | 279.80 | 1.932 | 0.3881 | 305.95 | 1.390 |
| 0.1214 | | 280.80 | 1.895 | 0.4049 | 306.95 | 1.375 |
| 0.1296 | | 282.00 | 1.855 | 0.4244 | 308.17 | 1.362 |
| 0.1377 | | 283.15 | 1.821 | 0.4441 | 309.25 | 1.345 |
| 0.1461 | | 284.40 | 1.795 | 0.4580 | 310.05 | 1.336 |
| 0.1568 | | 285.77 | 1.757 | 0.4804 | 311.15 | 1.317 |
| 0.1652 | | 286.82 | 1.731 | 0.5070 | 312.50 | 1.299 |
| 0.1727 | | 287.75 | 1.711 | 0.5355 | 313.75 | 1.277 |
| 0.1796 | | 288.55 | 1.692 | 0.5593 | 314.77 | 1.260 |
| 0.1872 | | 289.25 | 1.664 | 0.5870 | 315.90 | 1.241 |
| 0.1943 | | 290.25 | 1.659 | 0.6148 | 317.25 | 1.232 |
| 0.2010 | | 291.07 | 1.650 | 0.6530 | 318.55 | 1.204 |
| 0.2076 | | 291.65 | 1.630 | 0.7276 | 320.85 | 1.154 |
| 0.2149 | | 292.47 | 1.619 | 1.0000 | 327.15 | 1.000 |
| 0.2228 | | 293.60 | 1.623 | | | |
| Heptane | | | | | | |
| 0.0246 | | 272.50 | 6.823 | 0.2705 | 305.85 | 1.989 |
| 0.0344 | | 277.10 | 5.817 | 0.3222 | 308.25 | 1.798 |
| 0.0427 | | 280.10 | 5.247 | 0.3835 | 310.80 | 1.632 |
| 0.0520 | | 283.05 | 4.803 | 0.4372 | 312.60 | 1.511 |
| 0.0597 | | 284.95 | 4.479 | 0.5160 | 315.17 | 1.382 |
| 0.0763 | | 288.55 | 3.981 | 0.6009 | 317.75 | 1.279 |
| 0.0846 | | 290.25 | 3.813 | 0.6915 | 320.15 | 1.190 |
| 0.0992 | | 292.45 | 3.505 | 0.7666 | 321.87 | 1.127 |
| 0.1157 | | 294.45 | 3.216 | 0.8382 | 323.50 | 1.079 |
| 0.1337 | | 296.35 | 2.965 | 0.8634 | 324.05 | 1.064 |
| 0.1535 | | 298.10 | 2.736 | 0.9169 | 325.15 | 1.033 |
| 0.1747 | | 299.90 | 2.549 | 0.9624 | 326.25 | 1.014 |
| 0.1997 | | 301.75 | 2.367 | 1.0000 | 327.15 | 1.000 |
| 0.2290 | | 303.45 | 2.179 | | | |

### 2.2. Measurements

All the operations were done in purified argon atmosphere. The enthalpies of fusion and solubilities were determined as described in Part 1 [1]. All the direct experimental data are collected in Tables 2 and 3.

Table 4
Analysis of solubility data of compounds **A** and **B** by the Wilson, Wilson 3, UNIQUAC and NRTL equations (number of points in parentheses): values of parameters and deviations ($a$ in kJ mol$^{-1}$, $\Delta g$ in J mol$^{-1}$, $\sigma$ in K)

| Model and parameters | **A** | | **B** | |
|---|---|---|---|---|
| | Benzene (16) | Heptane (19) | Benzene (48) | Heptane (27) |
| Wilson | | | | |
| $\Delta g_{12}$ | −2497 | 6720 | −2320 | 1832 |
| $\Delta g_{21}$ | 4328 | 2324 | 4797 | 2965 |
| $\sigma$ | 0.67 | 3.97 | 1.29 | 1.51 |
| Wilson 3 | | | | |
| $a_{12} \times 10^{-3}$ | −0.7391 | 1.8741 | −0.6762 | 0.4107 |
| $a_{21} \times 10^{-3}$ | 1.2947 | 0.9803 | 1.4096 | 0.9829 |
| $\sigma$ | 1.03 | 2.74 | 1.45 | 1.37 |
| UNIQUAC | | | | |
| $\Delta g_{12}$ | 2481 | −718 | 2782 | 1001 |
| $\Delta g_{21}$ | −1158 | 2565 | −1020 | −105 |
| $\sigma$ | 0.99 | 6.46 | 1.75 | 1.85 |
| NRTL[a] | | | | |
| $\Delta g_{12}$ | 3470 | 52 | 2443 | 482 |
| $\Delta g_{21}$ | −1343 | 7842 | −1.7 | 3849 |
| $\sigma$ | 0.49 | 6.31 | 1.13 | 1.73 |

[a] Parameter $\alpha_{12} = 0.3$.

## 3. Results and discussion

The solubilities of compounds **A** and **B** in heptane and benzene are much lower than would be expected for ideal behaviour and show positive deviations from ideality ($\gamma_1 > 1$). The solubility of both compounds is higher in benzene than in heptane. Neither compound shows any phase transitions in the solid state, as proved by solubility and DSC measurements. The eutectic point in the system **B** + benzene was detected graphically: $x_{1e} = 0.079$, $T_{1e} = 274$ K. The equilibrium between the two forms of compound **B** has no significant influence on the solubility of this compound in hydrocarbons. Moreover, the differences between ideal solubility and experimental data are similar for both investigated compounds.

The solubility of a solid non-electrolyte 1 in a liquid solvent is expressed as

$$-\ln x_1 = \frac{\Delta H_{m1}}{R}\left(\frac{1}{T} - \frac{1}{T_{m1}}\right) + \ln \gamma_1 \qquad (1)$$

where $x_1$ is the mole fraction, $\gamma_1$ the activity coefficient, $\Delta H_{m1}$ the enthalpy of fusion, $T_{m1}$ the melting temperature and $T$ the equilibrium temperature of the solute, respectively.

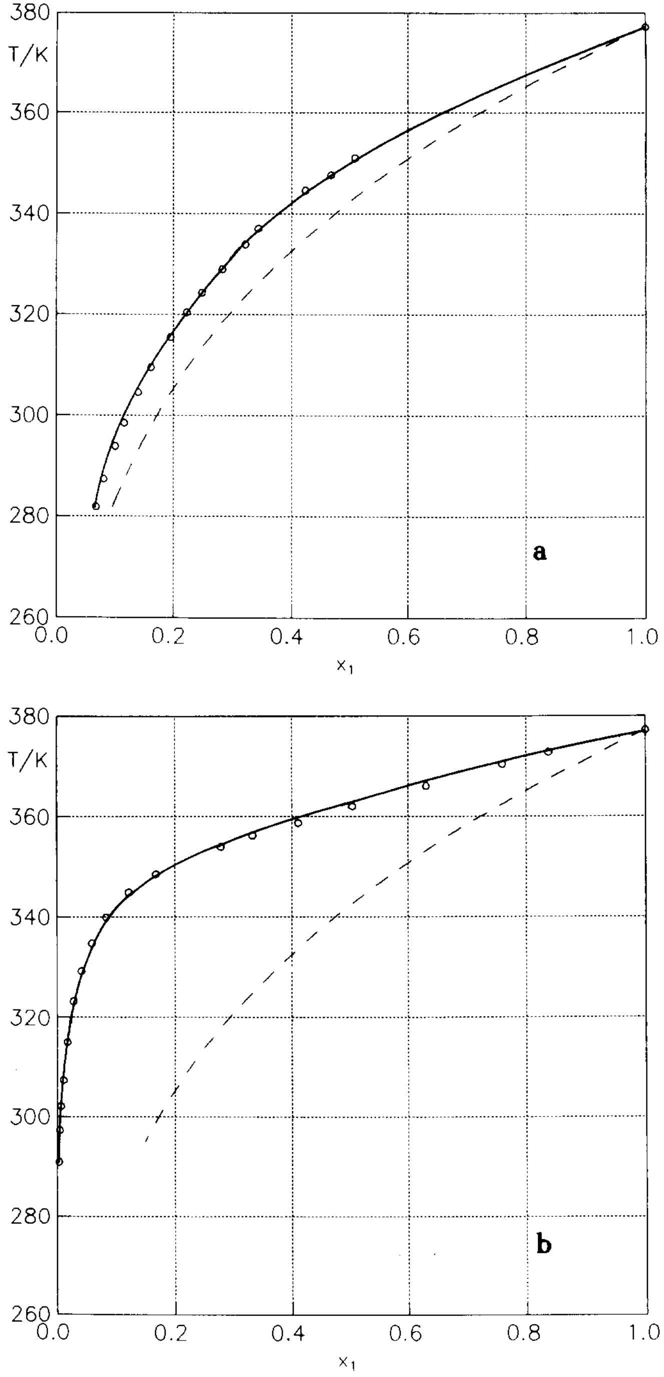


Fig. 1. Solubility of $[Et(AcO)B]_2O$ in benzene (a) and heptane (b). The experimental points are matched by curves calculated by the Wilson 3 equation. The dotted line represents the ideal solubility.

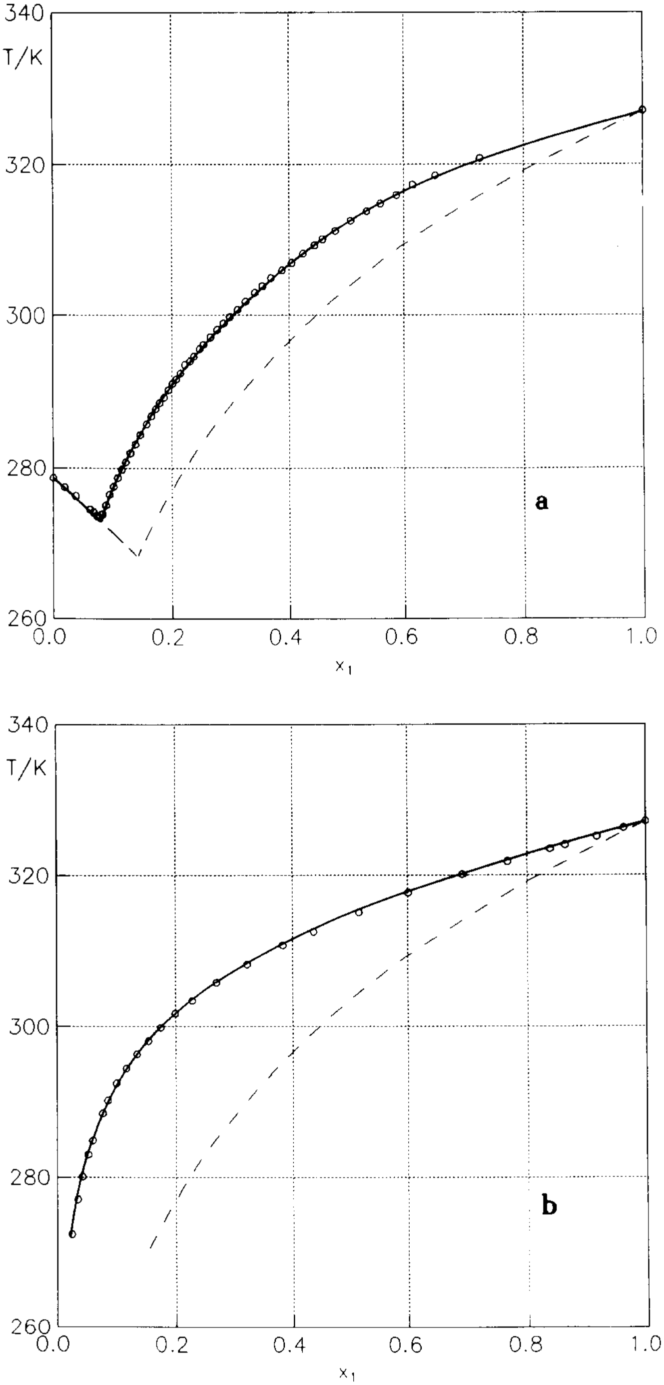


Fig. 2. Solubility of $[Et(CCl_3COO)B]_2O$ in benzene (a) heptane (b). The experimental points are matched by curves calculated by the Wilson 3 equation. The dotted line represents the ideal solubility.

In this study, only three methods were used to represent the solute activity coefficients ($\gamma_1$) from the correlation equations that describe the Gibbs excess free energy of mixing ($G^E$): the Wilson equation [8], the UNIQUAC model [9] and the NRTL model [10]. Two versions of the Wilson equation, i.e. $(g_{ij} - g_{ii}) \neq f(T)$ and $(g_{ij} - g_{ii}) = a_{ij}T^{-1}$ (W3) were applied. The constant of proportionality was similar to the non-randomness constant of the NRTL equation, $\alpha_{12} = 0.3$. The exact mathematical forms of the equations were presented in Ref. [11]. The pure component structural parameters $r$ (volume parameter) and $q$ (surface parameter), were obtained according to Refs. [11] and [12]. The parameters in the above relationship were fitted by an optimization technique. The objective function was

$$F(P_1 P_2) = \sum_{i=1}^{n} w_i^{-2}[\ln x_{1i}\gamma_{1i}(T_i x_{1i} P_1 P_2) - \ln a_{1i}(T_i)]^2 \qquad (2)$$

where ln $a_{1i}$ denotes an "experimental" value of the logarithm of solute activity, taken as the first term on the right hand side of Eq. (1), $w_i$ is the weight of an experimental point, described in Ref. [11], $P_1$, $P_2$ are the adjustable parameters of the correlation equation, $i$ denotes the $i$th experimental point, and $n$ is the number of experimental data.

The r.m.s. deviation of the temperatures defined by Eq. (3) was used as a measure of the solubility correlation

$$\sigma = \left[ \sum_{i=1}^{n} \frac{(T_i^{\exp} - T_i^{\mathrm{cal}})}{(n - l)} \right]^{1/2} \qquad (3)$$

where $T_i^{\exp}$ and $T_i^{\mathrm{cal}}$ are experimental and calculated temperatures of the $i$th point, respectively, $n$ is the number of experimental points (including the melting point) and $i$ is the number of adjustable parameters.

The calculated values of the equation parameters and corresponding r.m.s. deviations are presented in Table 4.

The best results for the correlation of experimental points in the tested binary systems were obtained by means of the Wilson equations, with the average r.m.s. deviations being 1.9 (Wilson) and 1.6 K (Wilson 3), see Figs. 1 and 2.

Further investigations of the structures of 1,3-diacyloxy-1,3-diethyl-1,3-diboroxanes and their equilibria in solutions are in progress.

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