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Solubilities of organoboron compounds in organic solvents. Part 4.[1] Solid–liquid equilibria of some pyrazaboles + methanol, ethanol, 2-propanol or *t*-butanol

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Abstract

The solubilities of some pyrazoboles (pyrazabole, 4,4,8,8-tetraethylpyrazabole (TEP), and 4,4,8,8-tetrapropylpyrazabole) in alkanols (methanol, ethanol, 2-propanol and *t*-butanol) have been determined at temperatures ranging from the boiling point of the solvent to 273 K. Two correlation methods were applied: the Wilson and UNIQUAC ASM model.

The best solubility correlation in alcohols was obtained with the UNIQUAC ASM KW equation, with the association constants as an adjustable parameter. In the calculations, the existence of one solid–solid first-order phase transition of TEP was also taken into consideration. The root-mean-square deviations of the solubility temperatures for all measured data varied from 2.9 to 1.9 K for the Wilson and UNIQUAC ASM models, respectively.

Keywords: Organoboron compounds; SLE; Solubility; UNIQUAC; Wilson

List of symbols

a_{12}	binary interaction parameter of the Wilson equation
ΔC_p	difference between heat capacities of the solute in the solid and liquid states
g_{ij}	molar energy of interaction between i and j
$\Delta g_{ij} = g_{ij} - g_{ii}$	difference between energies of interaction
$\Delta H_{\mathrm{m}1}$	molar enthalpy of fusion of the solute

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[1] For Part 3 see Ref. [1].

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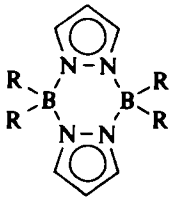
ΔH_{tr1}	molar enthalpy of the first solid–solid transition
ΔH°	enthalpy of hydrogen-bond formation
K_2	association constant, $(\phi_{2i+1}/\phi_{2i}\phi_{2M})[i/(i+1)]$
n	number of experimental points
l	number of adjustable parameters
R	universal gas constant
T^{exp}	experimental equilibrium temperature
T^{cal}	calculated equilibrium temperature
T_{m1}	melting point temperature of the pure solute
T_{tr1}	temperature of transition point
V_1, V_2	molar volume of the solute, solvent
x_1	molar fraction of the solute

Greek letters

γ_1	activity coefficient of the solute
Λ_{12}	parameter of the Wilson equations
ϕ_{2i}	segment fraction of alcohol i-mer
$\phi_{2\mathrm{m}}$	segment fraction of alcohol monomer
σ	r.m.s. deviation of temperature
Ω	objective function for the least-squares optimization

1. Introduction

The present work is a continuation of systematic studies on solid–liquid equilibria in new organic systems. In Parts 1 [2] and 2 [3], pyrazaboles with boron in a four-coordinated environment and containing heteroaromatic systems which would cause high chemical stability of these compounds [4], were chosen for investigation: see the formula below where R is H, Et, *n*-Pr.



A phase transition, with a high enthalpy of transformation, $\Delta H_{\mathrm{trl}} = 28.61\ \mathrm{kJ\ mol^{-1}}$ at the temperature $T_{\mathrm{trl}} = 342.30 \pm 0.15$ K was observed for 4,4,8,8-tetraethylpyrazabole (TEP). Recently, a polymorphic transition in the solid state [5] was discovered as a solid–solid phase transition below the melting point, this had not been reported for pyrazaboles.

The aim of the present work was to study the solubility of three selected pyrazaboles in strongly associated alcohols to investigate the influence of the structure of alcohols on solubility and to attempt a correlation of the experimental results with established theories of solutions.

2. Experimental

Pyrazabole (PYR), tetraethylpyrazabole (4,4,8,8-tetraethylpyrazabole) (TEP) and tetrapropylpyrazabole (4,4,8,8-tetrapropylpyrazabole) (TPP) were synthesized by Niedenzu according to [4]. The solvents were dried over 4A molecular sieves and fractionally distilled using a 35-plate laboratory column. The characteristics of the solutes and solvents are listed in Table 1. Solubilities were determined by a dynamic (synthetic) method, described in our previous paper [2]. The reproducibility of the measurements was 0.1 K, corresponding to a standard error in mole fraction δx_1 of 0.0005. All the experimental data (except in 2-propanol, published in Ref. [2]) are shown in Tables 2–4.

3. Results and discussion

The solubility of PYR, TEP and TPP in each solvent was lower than expected from ideal solution behaviour and the solution showed positive deviations from ideality ($\gamma_1 >> 1$). The solubilities of the solute were close to ideal values in the order: methanol < ethanol < 2-propanol < *t*-butanol.

All experimental activity coefficients are listed in Tables 2–4, and the solid–liquid equilibrium data are shown in comparison with the ideal solubility for a few systems in Figs. 1 and 2. Substitution of propyl groups in positions 4 and 8 of pyrazabole results in decreased solubility in each of the alcohols, compared to those of PYR and TEP. The boron heterocycles contain positive charges delocalized on the pyrazolyl ligand and negative charges on the boron atom of the BR_2 group. For the substituted pyrazaboles, TEP and TPP, an enhancement of this effect comparing with PYR and an increase in the intermolecular solute–solvent association may be expected. However, the molecular weight and size of the solute increases from PYR to TPP and has an influence in decreasing the solubility of the solids. Only the solubility of the β-crystalline form of TEP was close to that of PYR with decreasing self-association of alcohols, Figs. 3 and 4.

Table 1
Characteristics of solute and solvents

Substance	$V_m^{\circ a}/(\mathrm{cm^3\ mol^{-1}})$	n_D^b(at 298.15 K)	T_{m1}/K	$\Delta H_{tr1}/\mathrm{kJ\ mol^{-1}}$	$\Delta H_{m1}/\mathrm{kJ\ mol^{-1}}$
PYR	170.0		354.25		11.83
TEP	287.0		379.15	28.61	3.22
TPP	345.0		382.15		33.00
Methanol	40.8[c]	1.3297			
Ethanol	58.7[c]	1.3610			
2-Propanol	76.8[c]	1.3750			
t-Butanol	94.9[c]	1.3851			

[a] V_m° is the moplar volume at 298.15 K. [b] n_D is the refractive index. [c] Data from Ref. [6].

Table 2
Experimental mole fraction solubilities and activity coefficients of PYR

x_1	T_2/K	T_1/K	γ_1	x_1	T_1/K	γ_1
Methanol						
0.0299		275.75	10.660	0.1987	328.15	3.656
0.0315		279.55	10.854	0.2486	331.05	3.036
0.0413		289.65	9.886	0.2933	333.75	2.664
0.0641		303.45	7.964	0.3350	335.05	2.371
0.0890		312.35	6.556	0.3813	336.85	2.131
0.1209		319.75	5.362	1.0000	354.25	1.000
0.1568		323.95	4.380			
Ethanol						
0.0265		276.25	12.140	0.3774	334.55	2.092
0.0313		281.95	11.407	0.4478	336.85	1.815
0.0429		292.05	9.909	0.5102	339.05	1.637
0.0666		305.05	7.856	0.5740	340.95	1.490
0.0976		313.45	6.074	0.6046	342.75	1.445
0.1381		319.95	4.708	0.6431	343.35	1.369
0.1800		324.55	3.847	0.6921	344.75	1.293
0.2255		328.15	3.222	0.7371	346.75	1.244
0.2676		330.45	2.798	1.0000	354.25	1.000
0.3129		332.95	2.472			
t-Butanol						
0.0090	294.25			0.2843	325.35	2.462
0.0147	293.65			0.3365	327.95	2.153
0.0198	292.95			0.3945	330.55	1.901
0.0266		292.35	16.061	0.4548	332.95	1.701
0.0341		295.25	13.142	0.5326	336.35	1.516
0.0524		302.85	9.652	0.5627	337.65	1.459
0.0762		307.05	7.078	0.6393	341.45	1.346
0.1051		312.15	5.535	0.7148	343.85	1.239
0.1378		315.65	4.441	0.8119	347.45	1.139
0.1778		319.15	3.616	0.8739	349.35	1.082
0.2143		321.45	3.097	0.9444	352.25	1.035
0.2524		323.95	2.721	1.0000	354.25	1.000

The enhancement in the solubility of pyrazaboles from methanol through *t*-butanol, was due to a decrease in the self-association of these alcohols [6, 7], as expected, and can be seen in the results of the solubility measurements of PYR, TEP and TPP. The solubility of PYR decreased in alcohols from C_4 to C_{12}, but the solubility of TEP and TPP increased in the alcohols from C_4 to C_{12} [3].

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

$$-\ln x_1 = \frac{\Delta H_1}{R}\left(\frac{1}{T}-\frac{1}{T_{m1}}\right) - \frac{\Delta C_{pm1}}{R}\left[\ln\left(\frac{T}{T_{m1}}\right)+\frac{T_{m1}}{T}-1\right]+\ln\gamma_1 \qquad (1)$$

where x_1 is the mole fraction, γ_1 the activity coefficient, ΔH_{m1} the enthalpy of fusion, ΔC_{pm1} the solute heat capacity during the melting process, T_{m1} the melting

Table 3
Experimental mole fraction solubilities and activity coefficients of TEP

x_1	$T_{\beta 2}$/K	$T_{\beta 1}$/K	γ_1	x_1	$T_{\beta 1}$/K	$T_{\alpha 1}$/K	γ_1
Methanol							
0.0052		278.65	13.448	0.0764	328.85		7.454
0.0074		287.05	14.127	0.0926	330.55		6.530
0.0103		294.15	14.003	0.1119	331.85		5.654
0.0141		301.35	13.960	0.1344	333.15		4.924
0.0202		309.15	13.427	0.1618	334.15		4.234
0.0300		315.95	11.802	0.1921	334.85		3.652
0.0405		320.85	10.519	0.2277	335.55		3.156
0.0524		324.45	9.281	0.2641	336.45		2.805
0.0643		327.15	8.337	1.0000	379.15		1.000
Ethanol							
0.0141		286.95	7.380	0.2603	333.35		2.560
0.0218		297.55	7.677	0.3095	334.55		2.244
0.0310		305.15	7.438	0.3602	335.45		1.988
0.0417		311.15	7.043	0.4144	335.75		1.746
0.0596		317.45	6.291	0.4914	337.55		1.564
0.0812		321.95	5.465	0.5346	337.65		1.443
0.1075		325.75	4.742	0.5980	338.45		1.325
0.1365		328.35	4.099	0.6734	339.65		1.225
0.1743		330.35	3.445	1.0000	379.15		1.000
0.2104		331.85	3.007				
t-Butanol							
0.0095	292.55			0.2733	325.45		1.845
0.0141	292.05			0.3145	327.45		1.723
0.0186	292.45			0.4033	330.75		1.510
0.0242		292.05	5.428	0.5083	333.85		1.334
0.0360		299.15	4.980	0.6118	336.85		1.227
0.0594		305.75	3.979	0.6750	338.75		1.186
0.0858		310.35	3.316	0.7505	339.85		1.106
0.1160		314.75	2.914	0.7560	340.05		1.105
0.1496		318.05	2.564	0.7941	340.85		1.080
0.1816		320.75	2.337	0.8290		348.15	1.101
0.2166		322.75	2.110	0.8388		354.15	1.109
0.2558		324.65	1.915	1.0000		379.15	1.000

temperature and T the equilibrium temperature of the solute. If the solid–solid transition occurs before fusion, an additional term must be added to the right-hand side of Eq. (1) [8, 9]

$$-\ln x_1 = \frac{\Delta H_1}{R}\left(\frac{1}{T}-\frac{1}{T_{m1}}\right) - \frac{\Delta C_{pm1}}{R}\left[\ln\left(\frac{T}{T_{m1}}\right)+\frac{T_{m1}}{T}-1\right] + \frac{\Delta H_{tr1}}{R}\left(\frac{1}{T}-\frac{1}{T_{tr1}}\right)+\ln\gamma_1 \qquad (2)$$

where ΔH_{tr1} and T_{tr1} are the enthalpy and temperature of the solid–solid transition of the solute. The quantitative fit of the solid–liquid equilibrium of Eqs. (1) and (2) has not

Table 4
Experimental mole fraction solubilities and activity coefficients of TPP

x_1	T_2/K	T_1/K	γ_1	x_1	T_1/K	γ_1
Methanol						
0.0019		279.25	11.459	0.0050	315.45	22.248
0.0021		288.55	16.392	0.0081	324.85	19.765
0.0025		297.35	20.687	0.0115	334.05	19.490
0.0035		306.45	21.964	1.0000	382.15	1.000
Ethanol						
0.0031		278.05	6.605	0.0236	327.85	7.586
0.0049		289.25	7.263	0.0356	337.35	7.072
0.0074		298.95	7.506	0.0528	345.05	6.200
0.0115		311.05	8.096	0.0790	350.85	5.012
0.0167		320.75	8.200	1.0000	382.15	1.000
t-Butanol						
0.0035	294.85			0.0351	315.95	3.2329
0.0058	294.55			0.0517	322.45	2.8274
0.0074	294.35			0.0745	328.45	2.4568
0.0105		293.35	4.1058	0.1024	335.25	2.2839
0.0125		294.75	3.6778	0.1334	340.75	2.1224
0.0141		295.65	3.3969	0.1608	344.15	1.9754
0.0159		298.15	3.3713	0.1932	348.15	1.8771
0.0184		301.45	3.3702	0.2341	352.75	1.7975
0.0218		303.75	3.1428	1.0000	382.15	1.0000

been tested for the pyrazaboles, because sufficiently accurate thermodynamic data are not available, e.g. for ΔC_{pm1}. Therefore, for the systems investigated the simplified version of the solubility equations was applied without a ΔC_{pm1} correction in Eq. (1) for temperatures above the temperature of transition and Eq. (2) at lower temperatures. Experimental values of the temperatures of the solid–solid phase transition were determined from solubility curves and DSC measurements (Table 1). Two methods were used to represent the solute activity coefficients (γ_1) from the so-called correlation equations describing the excess Gibbs free energy of mixing (G^E): the Wilson equation [10] and the UNIQUAC associated-solution model [11]. Five correlation methods were applied in our first paper [1]: the Wilson, UNIQUAC, NRTL, UNIQUAC ASM and modified NRTL1 equations but the best results were obtained with the Wilson equation and in alcohol with the UNIQUAC ASM KW (with the Kretschmer–Wiebe association model). The exact mathematical forms of the equations are given in Ref. [12]. The calculations with the UNIQUAC associated-solution model (UNIQUAC ASM) were carried out using K_2 values as the association constant for *n*-alkanols at 323.15 K, with the hydrogen-bond formation enthalpy ΔH° according to Nagata [7] and presented in Table 5. The results for 2-propanol [2] were recalculated, and gave a better solubility correlation. In addition, calculations with K_2 as the third adjustable parameter were also made using the Kretschmer–Wiebe model of association. The pure component structural parameters *r* (volume parameter) and *q* (surface parameter) were obtained according to

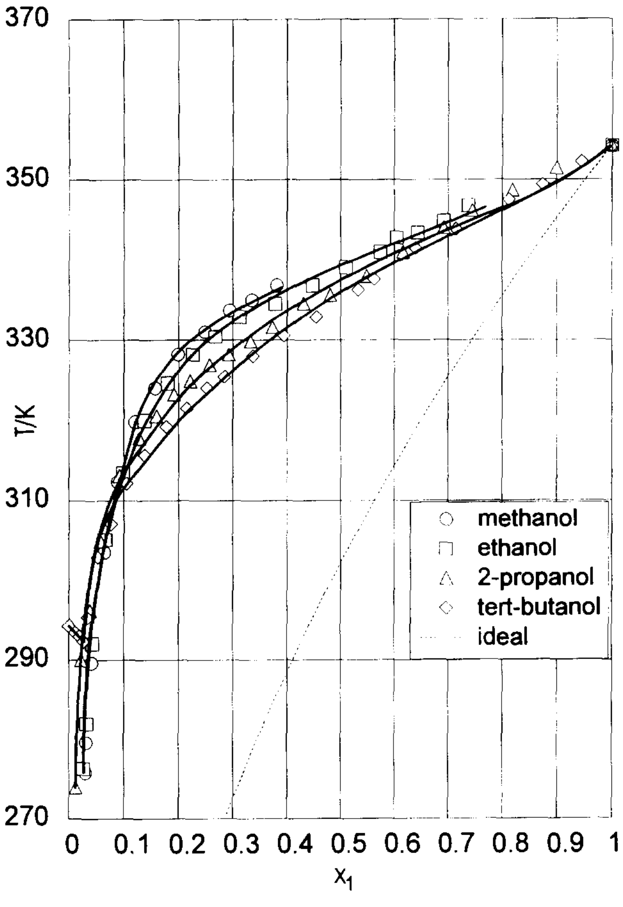


Fig. 1. Solubility of PYR in methanol, ethanol, 2-propanol, and *t*-butanol. The dotted line represents the ideal solubility.

Refs. [12, 13]. The temperature dependence of the association constant was calculated from the van't Hoff relation assuming the enthalpy of hydrogen-bond formation to be temperature independent. The parameters of the equations were found by an optimization technique using the maximum neighbourhood method for minimization

$$\Omega = \sum_{i=1}^{n} [T_i^{\mathrm{exp}} - T_i^{\mathrm{cal}}(x_1, P_1, P_2)]^2 \tag{3}$$

where T_i^{exp} denotes an experimental value of the temperature for a given concentration x_{1i}, T_i^{cal} is the temperature calculated for a given concentration x_{1i}, and parameters P_1 and P_2 were obtained by solving the non-linear equation (Eq. (1) or (2)), depending on the temperature and the expression for the logarithm of the activity according to the assumed model. The non-linear equations were solved using the secant method. The r.m.s. deviation of the temperatures defined by Eq. (4) was used as a measure of the

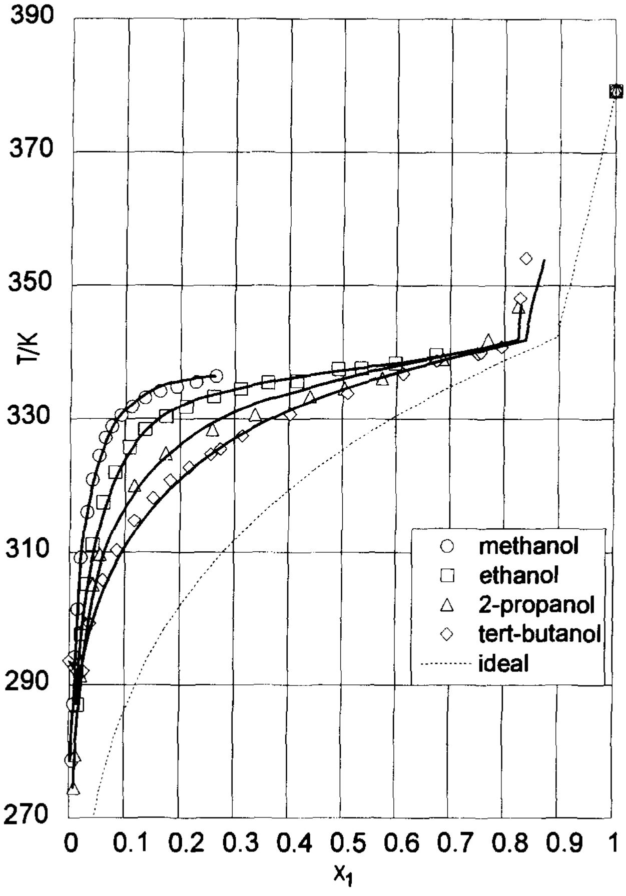


Fig. 2. Solubility of TEP in methanol, ethanol, 2-propanol, and *t*-butanol. The dotted line represents the ideal solubility.

goodness of fit

$$\sigma = \left[\sum_{i=1}^{n} \frac{(T_i^{\exp} - T_i^{\mathrm{cal}})^2}{(n-l)}\right]^{1/2} \tag{4}$$

where n is the number of experimental points (including the melting point) and l is the number of adjustable parameters.

The Wilson equation has been tested with a parameter Λ_{12} in the form

$$\Lambda_{12} = (V_2/V_1)\exp[-(g_{12} - g_{11})/RT] \tag{5}$$

where

$$(g_{12} - g_{11}) = \frac{a_{12}}{T}; \quad a_{12} \neq f(T) \tag{6}$$

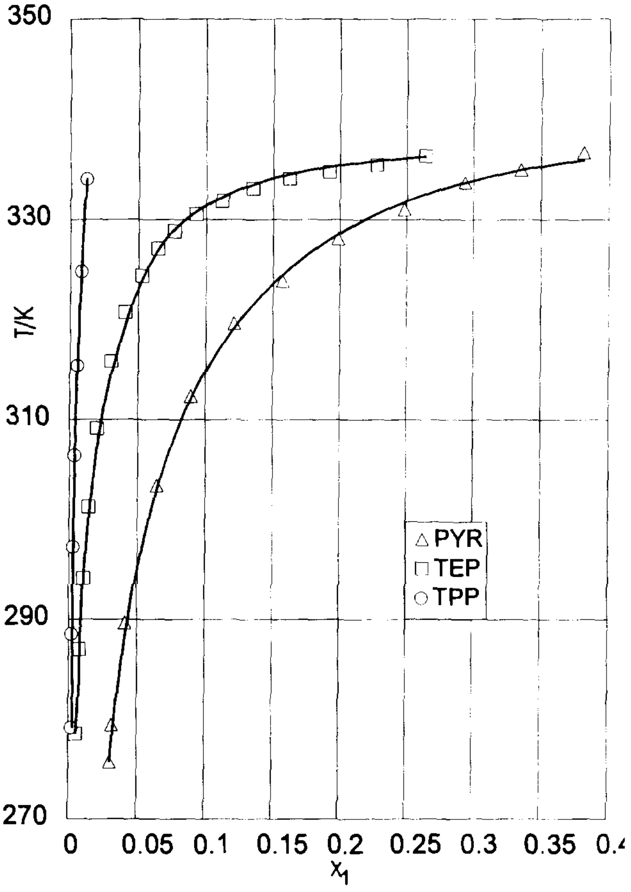


Fig. 3. Solubility of PYR, TEP and TPP in methanol. The experimental points are fitted to the equations given in the text.

Table 5
Association parameters of alcohols [11]

Alcohol	K(at 323.15 K)	$-\Delta H^\circ$/kJ mol
Methanol	125.1	23.6
Ethanol	103.2	23.6
2-Propanol	71.9	23.9
t-Butanol	30.5	21.5

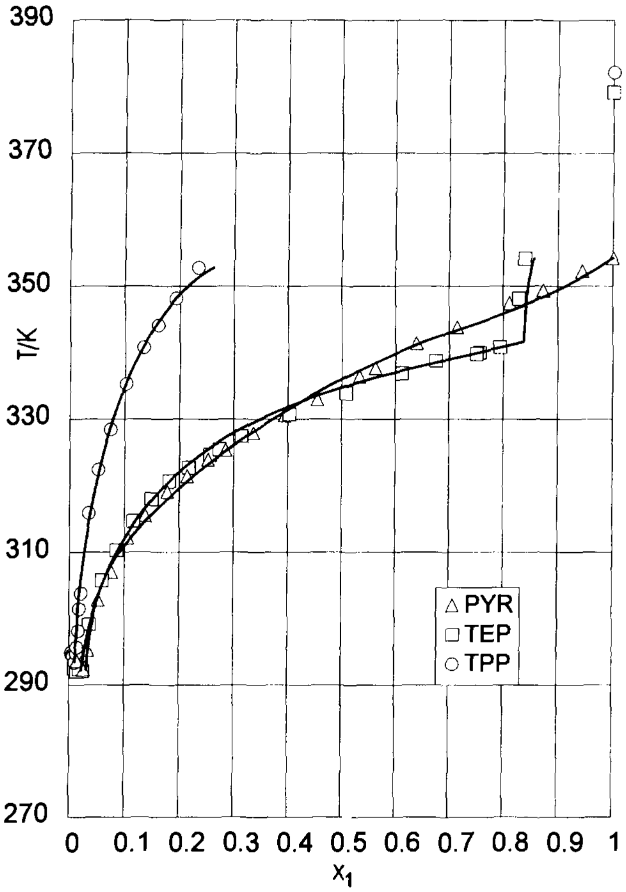


Fig. 4. Solubility of PYR, TEP and TPP in *t*-butanol. Experimental points are matched by curves calculated by the UNIQUAC ASM KW equation.

V_1, V_2 are the molar volumes of pure solute and solvent in the liquid phase and g_{12} is the molar energy of interaction between the 1 and 2 components; a_{12} is the binary interaction parameter.

Table 6 lists the results of fitting the solubility curves by the Wilson equation and Table 7 by the UNIQUAC ASM KW equation. For the twelve systems, the description of the solid-liquid equilibria was given by the Wilson equation with the average r.m.s. deviation 2.9 K. Taking into consideration the association of *n*-alkanols in the form of the UNIQUAC ASM KW, a similar mathematical description is observed for all the systems ($\sigma = 1.9$ K).

The best solubility correlation in alcohols was obtained with the UNIQUAC ASM KW, with the association constant as an adjustable parameter. In this case the average r.m.s. deviation is reduced to $\sigma = 1.5$ K.

Table 6
Analyses of solubility data of pyrazaboles in four alcohols by the Wilson equation; values of the parameters and measures of deviations (Δg in J mol^{-1}; σ in K)

Solvent	PYR	TEP	TPP
Methanol			
$a_{12} \times 10^{-3}$	0.8937	−0.0217	−0.3422
$a_{21} \times 10^{-3}$	8.2674	9.4648	115.3349
σ	0.83	1.28	5.38
Ethanol			
$a_{12} \times 10^{-3}$	1.8935	−0.3916	−1.5522
$a_{21} \times 10^{-3}$	7.2500	7.6656	11.0506
σ	2.23	0.89	1.98
2-Propanol			
$a_{12} \times 10^{-3}$	1.1572	−0.1314	−0.5405
$a_{21} \times 10^{-3}$	1.7264	1.9324	2.3659
σ	3.76	7.43	2.32
t-Butanol			
$a_{12} \times 10^{-3}$	4.5004	0.5067	−0.7361
$a_{21} \times 10^{-3}$	4.3658	4.0968	4.1281
σ	3.79	3.70	1.23

Table 7
Analyses of solubility data of pyrazaboles in four alcohols by the UNIQUAC ASM KW equation; values of the parameters and measures of deviations (Δg in J mol^{-1}; σ in K)

Solvent	PYR	TEP	TPP
Methanol			
Δg_{12}	1234.14	2533.88	5562.82
Δg_{21}	−751.04	−1515.43	−2137.47
σ	0.69	0.89	4.05
Δg_{12}	1416.57	3447.41	9257.95
Δg_{21}	−852.88	−1724.77	−2232.79
K_2	111.91	55.26	40.02
σ	0.71	0.80	3.76
Ethanol			
Δg_{12}	−993.67	−902.90	−1687.43
Δg_{21}	1754.29	1077.09	3564.03
σ	0.73	1.43	1.79
Δg_{12}	−1002.95	3065.75	3840.08
Δg_{21}	1769.64	−1714.76	−1990.82
K_2	103.93	28.86	40.74
σ	0.71	0.67	1.10
2-Propanol			
Δg_{12}	−1687.43	426.38	−537.49
Δg_{21}	3564.03	−465.68	418.74
σ	1.83	2.55	1.66
Δg_{12}	−1704.58	−1294.05	−1945.95
Δg_{21}	3604.68	1726.87	2884.25
K_2	76.34	31.12	55.22
σ	1.79	1.97	0.56

Table 7 (*Continued*)

Solvent	PYR	TEP	TPP
t-Butanol			
Δg_{12}	−1592.85	320.71	475.45
Δg_{21}	3383.15	−376.79	−619.84
σ	1.51	3.93	1.78
Δg_{12}	−1729.21	−1920.77	133.06
Δg_{21}	3695.15	3153.38	−261.59
K_2	49.19	18.97	17.48
σ	1.10	3.39	1.08

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