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Solubilities of organoboron compounds in organic solvents. Part 2. Solid–liquid equilibria of some pyrazaboles + n-alkanols

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Abstract

The solubilities of some pyrazaboles (pyrazabole, 4,4,8,8-tetraethylpyrazabole, and 4,4,8,8-tetrapropylpyrazabole) in n-alkanols (1-butanol, 1-hexanol, 1-octanol, 1-decanol and 1-dodecanol) have been determined at temperatures ranging from the melting point of the solute to 273 K. Two correlation methods were applied: the Wilson and the UNIQUAC ASM [associated-solution model].

The average r.m.s. deviations of the solubility temperatures for all measured data were 1.8 K and 2.0 K for the Wilson and the UNIQUAC ASM model respectively. The best solubility correlation for 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 4,4,8,8-tetraethylpyrazabole has also been taken into consideration.

Keywords: Organoboron compound; 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

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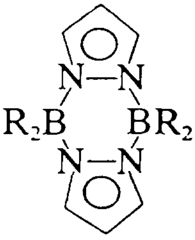
g_{ij}	Molar energy of interaction between *i* and *j*
$\Delta g_{ij} = g_{ij} - g_{ii}$	Difference between energies of interaction
ΔH_{m1}	Molar enthalpy of fusion of solute
ΔH_{tr1}	Molar enthalpy of the first solid–solid transition
h_2	Enthalpy of hydrogen bond formation
K_2	Association constant, $(\phi_{2i+1}/\phi_{2i}\phi_{2M})[i/(i+1)]$
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 solute, solvent
x_1	Molar fraction of solute

Greek letters

γ_1	Activity coefficient of solute
Λ_{12}	Parameter of the Wilson equations
ϕ_{2i}	Segment fraction of alcohol i-mer
ϕ_{2m}	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. This is the second publication for such systems reporting the solubilities of organoboron compounds. In Part 1 [1] the pyrazaboles, in which boron exists in a four-coordinated environment and the presence of a heteroaromatic system confers high chemical stability on the compounds [2], were chosen for investigation (see Formula 1, where R is H, Et or *n*-Pr).



Formula 1.

The solubilities of these pyrazaboles in heptane and 2-propanol have been determined [1]. The solubilities in alcohol were close to or lower than those in heptane. This suggests that the solids under study are not able to form stable complexes in solution with polar solvents. Phase transition with a high enthalpy of transformation ($\Delta H_{\mathrm{tr1}} = 28.61$ kJ mol^{-1}) at temperature $T_{\mathrm{tr1}} = 342.30 \pm 0.15$ K was observed for 4,4,8,8-tetraethylpyrazabole (TEP) in both solvents [1]. We have suggested a boat → chair ($\beta \rightarrow \alpha$) conformation change. Solid–solid phase transition below the melting point has never been reported for pyrazaboles.

The first X-ray analysis of the crystal and molecular structure of a pyrazabole was reported for the species H(pz')B(pz')$_2$BH(pz'), where pz' is 3,5-dimethylpyrazolyl [3]. The compound was found to exist with a chair conformation of the central B_2N_4 ring having the two terminal pyrazolyl groups in the trans arrangement. Later, pyrazaboles were found to exist in boat, chair or planar conformation of the B_2N_4 ring, and no steric influence of the terminal substituents was confirmed [4]. Rather, the individual structures of pyrazaboles seem to result from crystal packing effects. The simplest pyrazabole (PYR), in which R is H, exists in a boat conformation of the central B_2N_4 ring [5]. In order to determine the crystal and molecular structure of α and β forms of TEP, investigations are currently in progress by NMR spectroscopy, adiabatic calorimetry and X-ray spectroscopy [6].

The aim of this work was to study the solubility of three selected pyrazaboles in aliphatic alcohols (C_4–C_{12}) and to attempt a correlation of all the experimental results with the established theories of solutions.

2. Experimental

2.1. Materials

Pyrazabole (PYR), tetraethylpyrazabole (4,4,8,8-tetraethylpyrazabole, TEP) and tetrapropylpyrazabole (4,4,8,8-tetrapropylpyrazabole, TPP) were donated by Niedenzu [2]. The solvents were dried over 4A molecular sieves (BDH, Poole, UK) and fractionally distilled through a 35-plate laboratory column. The characteristics of the solutes and solvents are listed in Table 1.

The solubilities were determined by a dynamic (synthetic) method as described in Part 1 [1].

The reproducibility of the measurements was 0.1 K, which corresponds to a standard error in composition δx_1 of 0.0005. All the direct experimental data are shown in Tables 2–4.

3. Results and discussion

The solubility of PYR in each solvent is much lower than would be expected for ideal behaviour, and shows positive deviations from ideality ($\gamma_1 \gg 1$). The solubilities of TPP and, especially, of TEP are close to the ideal values in 1-dodecanol and are lower than the ideal values in the other solvents ($\gamma > 1$).

Table 1
Characteristics of solutes and solvents

Substance	$V_m^\ominus$ [a]/(cm^3 mol^{-1})	n_D [b] (at 298.15 K)	T_{m1}/K	ΔH_{m1}/(kJ mol^{-1})
PYR	170.0		354.25 [c]	11.83
TEP	287.0		379.15 [d]	3.22
TPP	345.0		382.15	33.00
1-Butanol	92.00 [e]	1.3973		
1-Hexanol	125.30 [e]	1.4164		
1-Octanol	158.50 [e]	1.4296		
1-Decanol	191.60 [e]	1.4360		
1-Dodecanol	224.70 [e]	1.4402		

[a] $V_m^\ominus$ is the molar volume at 298.15 K. [b] n_D is the refractive index. [c] T_{m1} = 353.15–354.15 K [7]. [d] T_{m1} = 379.15–380.15 K [7]. [e] Data from Ref. [8].

Table 2
Experimental mole fraction solubilities x_1 and activity coefficients γ_1 of PYR

x_1	T_1/K	γ_1	x_1	T_1/K	γ_1
1-Butanol					
0.0246	273.45	12.406	0.2955	327.95	2.452
0.0318	282.95	11.429	0.3392	329.85	2.190
0.0377	288.25	10.575	0.3931	332.05	1.945
0.0455	292.95	9.484	0.4451	334.15	1.764
0.0715	304.35	7.239	0.5217	336.65	1.554
0.1027	311.55	5.615	0.5872	338.15	1.407
0.1306	315.95	4.705	0.6732	341.05	1.272
0.1596	318.95	4.017	0.7720	344.95	1.162
0.1881	321.55	3.534	0.8480	347.55	1.091
0.2185	323.75	3.135	0.9124	350.65	1.052
0.2547	326.15	2.778	1.0000	354.25	1.000
1-Hexanol					
0.0255	275.35	12.406	0.4013	333.45	1.940
0.0412	287.45	9.544	0.4979	336.35	1.622
0.0604	296.75	7.603	0.6256	340.95	1.367
0.0893	307.55	6.085	0.7597	345.65	1.191
0.1289	314.25	4.653	0.8325	348.35	1.122
0.1751	319.75	3.703	0.8897	349.95	1.070
0.2290	324.25	3.011	0.9519	352.45	1.029
0.3076	328.95	2.387	1.0000	354.25	1.000
1-Octanol					
0.0262	273.85	11.737	0.3092	330.05	2.409
0.0296	277.55	11.134	0.3849	332.75	2.004
0.0334	281.25	10.556	0.4683	335.25	1.701
0.0486	293.25	8.923	0.5774	338.85	1.443
0.0769	302.55	6.546	0.7158	343.65	1.234
0.1087	310.25	5.205	0.7864	346.35	1.160
0.1435	316.55	4.319	0.8911	349.75	1.066
0.1840	321.95	3.632	1.0000	354.25	1.000
0.2401	326.65	2.966			

Table 2 (continued)

x_1	T_2/K	T_1/K	γ_1	x_1	T_1/K	γ_1
1-Decanol						
0.0000	280.15			0.3451	332.95	2.241
0.0163	279.65			0.3925	334.65	2.014
0.0180	279.45			0.4462	336.35	1.810
0.0208	279.40			0.5408	339.15	1.546
0.0229	279.35			0.5915	340.45	1.437
0.0246	279.30			0.5940	340.95	1.439
0.0259	279.25			0.6281	341.05	1.363
0.0290		278.65	11.597	0.6604	341.85	1.309
0.0302		279.15	11.239	0.6773	342.25	1.283
0.0312		279.95	11.038	0.6899	342.85	1.268
0.0380		285.15	9.943	0.7292	343.95	1.216
0.0627		297.85	7.455	0.7748	345.45	1.165
0.0890		306.55	6.014	0.7821	346.15	1.164
0.1182		313.35	5.008	0.8367	347.85	1.110
0.1515		318.35	4.196	0.8569	348.35	1.090
0.1963		323.15	3.461	0.9084	350.55	1.055
0.2379		326.65	2.994	0.9375	351.85	1.038
0.2901		329.95	2.564	1.0000	354.25	1.000
1-Dodecanol						
0.0000	297.15			0.2872	330.65	2.614
0.0248	296.35			0.3366	333.15	2.304
0.0316	296.25			0.3845	335.25	2.071
0.0440	296.15			0.4405	337.25	1.854
0.0505		296.15	9.005	0.5017	339.05	1.665
0.0689		302.75	7.329	0.5852	341.25	1.466
0.0869		307.15	6.216	0.6777	343.35	1.299
0.1059		311.45	5.437	0.7662	345.95	1.185
0.1299		315.15	4.677	0.8341	348.35	1.120
0.1605		320.35	4.073	0.8890	349.65	1.067
0.1986		324.85	3.501	0.9443	351.95	1.032
0.2416		327.85	2.995	1.0000	354.25	1.000

All the 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 Fig. 1(a)–(d). TEP in the β crystalline form has the highest solubility in most of the alcohols in comparison with PYR and TPP (see Fig. 2). Only in 1-butanol and 1-hexanol is the solubility of TEP close to that of PYR. Substitution of propyl groups in positions 4 and 8 of pyrazabole results in a decrease in solubility for each alcohol involved compared with PYR and TEP. The structure of boron heterocycles contains positive charges delocalized on the pyrazolyl ligand and negative charges on the boron atom in the BR_2 group. For the substituted pyrazaboles TEP and TPP, an enhancement of this effect compared with PYR and an increase in the intermolecular solute–solvent association may be expected. However, the molecular weight and the size of solute increases on passing from PYR to TPP and has an influence on the decreasing solubility of the solids. The results of measurements have shown that only TEP has higher solubility than PYR in some alcohols and this is mainly the effect of the different crystalline form α of TEP.

The enhancement of the solubility of pyrazaboles on passing from 1-butanol to 1-dodecanol, according to the decrease in self-association of these alcohols [9,10], is

Table 3
Experimental mole fraction solubilities and activity coefficients of TEP

x_1	$T_{\beta 1}/\mathrm{K}$	γ_1	x_1	$T_{\beta 1}/\mathrm{K}$	$T_{\alpha 1}/\mathrm{K}$	γ_1
1-Butanol						
0.0177	274.55	3.218	0.2679	329.15		2.148
0.0209	280.75	3.708	0.3267	330.25		1.831
0.0286	288.65	3.936	0.3752	332.15		1.704
0.0397	297.35	4.179	0.4406	333.35		1.513
0.0543	303.05	3.893	0.5457	335.35		1.308
0.0726	309.55	3.796	0.5994	336.35		1.232
0.0808	311.55	3.693	0.6579	337.25		1.157
0.0937	315.15	3.664	0.6960	338.75		1.150
0.1180	318.45	3.300	0.7394	339.15		1.097
0.1241	318.95	3.197	0.7884	341.25		1.103
0.1441	321.45	3.023	0.8432	342.65		1.064
0.1750	323.85	2.719	0.9023		362.95	1.059
0.1790	324.65	2.737	1.0000		379.15	1.000
0.2190	326.75	2.413				
1-Hexanol						
0.0201	274.35	2.805	0.4241	331.85		1.492
0.0243	279.35	2.979	0.5058	333.35		1.318
0.0390	290.05	3.077	0.5758	334.95		1.223
0.0581	296.95	2.807	0.6090	335.55		1.180
0.0817	304.15	2.708	0.7313	337.85		1.062
0.1343	314.25	2.469	0.7976	339.35		1.024
0.1770	319.35	2.276	0.8265	340.05		1.011
0.2042	322.05	2.181	0.8741		343.65	1.029
0.2162	322.95	2.129	0.9003		357.25	1.043
0.2772	326.45	1.886	0.9414		366.75	1.026
0.3485	330.05	1.705	1.0000		379.15	1.0000
1-Octanol						
0.0245	273.55	2.209	0.5142	334.75		1.360
0.0261	276.65	2.426	0.5979	335.95		1.218
0.0375	283.65	2.376	0.6753	337.55		1.138
0.0557	292.35	2.390	0.7450	338.45		1.064
0.0748	299.85	2.470	0.8223	340.65		1.037
0.0986	305.25	2.348	0.8509		346.95	1.069
0.1345	313.65	2.409	0.8753		355.45	1.067
0.1785	317.85	2.132	0.9042		362.45	1.055
0.2421	322.35	1.860	0.9213		367.25	1.050
0.3248	327.55	1.674	1.0000		379.15	1.000
0.4217	332.25	1.521				

Table 3 (continued)

x_1	$T_{\beta 2}$/K	$T_{\beta 1}$/K	γ_1	x_1	$T_{\beta 1}$/K	$T_{\alpha 1}$/K	γ_1
1-Decanol							
0.0000	280.15			0.3508	327.15		1.528
0.0144	273.15			0.3995	329.05		1.436
0.0158	273.15			0.4580	331.15		1.348
0.0191	273.15			0.5235	333.95		1.300
0.0226	273.15			0.5926	335.15		1.196
0.0277		278.95	2.562	0.5952	335.35		1.199
0.0300		279.55	2.436	0.6478	335.95		1.124
0.0493		287.05	2.120	0.6894	336.85		1.089
0.0762		296.75	2.121	0.7197	337.35		1.061
0.1052		305.15	2.192	0.7294	337.65		1.058
0.1338		309.45	2.052	0.7559	338.45		1.048
0.1604		312.85	1.958	0.7986	339.45		1.026
0.1826		315.55	1.909	0.8116	339.85		1.023
0.2113		318.05	1.815	0.8464	340.55		1.004
0.2403		320.35	1.740	0.9203		359.55	1.028
0.2717		322.65	1.676	0.9574		364.75	1.003
0.3053		324.85	1.616	1.0000		379.15	1.000
1-Dodecanol							
0.0000	297.15			0.4870	331.55		1.286
0.0306	296.85			0.5844	334.65		1.192
0.0655	296.05			0.6814	336.75		1.098
0.0792		295.95	1.971	0.7434	337.85		1.045
0.1070		305.95	2.227	0.7897	338.75		1.013
0.1370		309.75	2.028	0.8084	339.25		1.007
0.1432		310.05	1.963	0.8088	339.45		1.013
0.1662		313.05	1.904	0.8558	339.95		0.973
0.1999		316.25	1.792	0.9005		345.15	1.004
0.2486		320.35	1.682	0.9158		352.15	1.010
0.2519		320.15	1.648	0.9698		370.75	1.008
0.3114		323.95	1.534	1.0000		379.15	1.000
0.3880		328.25	1.437				

also to be expected. It was confirmed by the results of solubility measurements on TEP and TPP. The solubility of PYR decreases in the tested alcohols from C_4 to C_{12}, but on the other hand the solubility of TEP and TPP increases going from C_4 to C_{12} alcohols as shown in Fig. 3(a) and (b). Thus, the simple pyrazabole (PYR) in which R is H does not show special solute–solvent interaction and no influence of decreasing self-association of *n*-alcohols is observed.

The substituted pyrazaboles TEP and TPP show stronger solute–solvent interaction, especially in 1-dodecanol.

There must be also a negative contribution to the activity coefficient reflecting the construction of the orientational order in the solutions of TEP and TPP with *n*-alkanols and revealing positive deviations from ideality. The combinatorial effects (combinatorial entropy) play a large role in many systems: long-chain paraffins + cycloalkane, long-chain paraffins + long-chain solvents and others [11].

The eutectic points in six systems were determined graphically: for 1-decanol, $x_{1c} = 0.029$, $T_{1c} = 278.6$, $x_{1e} = 0.024$, $T_{1e} = 278.5$, $x_{1c} = 0.011$, $T_{1e} = 279.3$; and for 1-dodecanol, $x_{1e} = 0.050$, $T_{1c} = 296.1$, $x_{1c} = 0.079$, $T_{1e} = 295.9$, $x_{1e} = 0.034$, $T_{1e} = 296.9$ for PYR, TEP and TPP, respectively.

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

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

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

Table 4
Experimental mole fraction solubilities and activity coefficients of TPP

x_1	T_1/K	γ_1	x_1	T_1/K	γ_1
1-Butanol					
0.0085	275.35	2.094	0.1578	347.95	2.283
0.0097	278.55	2.166	0.1914	351.55	2.116
0.0116	281.85	2.140	0.2299	355.05	1.969
0.0148	289.55	2.439	0.2680	358.15	1.860
0.0222	301.05	2.745	0.3232	362.45	1.759
0.0371	314.75	2.916	0.3557	364.35	1.693
0.0523	324.25	2.993	0.3994	365.85	1.576
0.0787	334.75	2.920	0.4450	368.05	1.510
0.1034	340.85	2.747	0.5088	370.25	1.408
0.1273	344.45	2.520	1.0000	382.15	1.000
1-Hexanol					
0.0131	277.05	1.485	0.1876	347.35	1.883
0.0142	281.45	1.713	0.2298	352.35	1.808
0.0195	287.85	1.707	0.2905	357.35	1.674
0.0298	301.05	2.045	0.3585	361.45	1.539
0.0446	311.25	2.105	0.4151	364.35	1.450
0.0667	321.75	2.134	0.4968	368.15	1.356
0.0850	327.95	2.114	0.5562	369.25	1.251
0.1033	333.35	2.116	0.6220	371.25	1.185
0.1244	337.45	2.031	1.0000	382.15	1.000
0.1514	342.55	1.988			
1-Octanol					
0.0119	274.75	1.450	0.2717	353.25	1.574
0.0200	285.95	1.519	0.3393	357.55	1.442
0.0357	300.95	1.699	0.4273	361.85	1.307
0.0571	314.35	1.864	0.5273	366.35	1.212
0.0924	328.75	2.003	0.6259	369.85	1.131
0.1374	337.65	1.852	0.6721	371.15	1.094
0.2004	346.45	1.711	1.0000	382.15	1.000

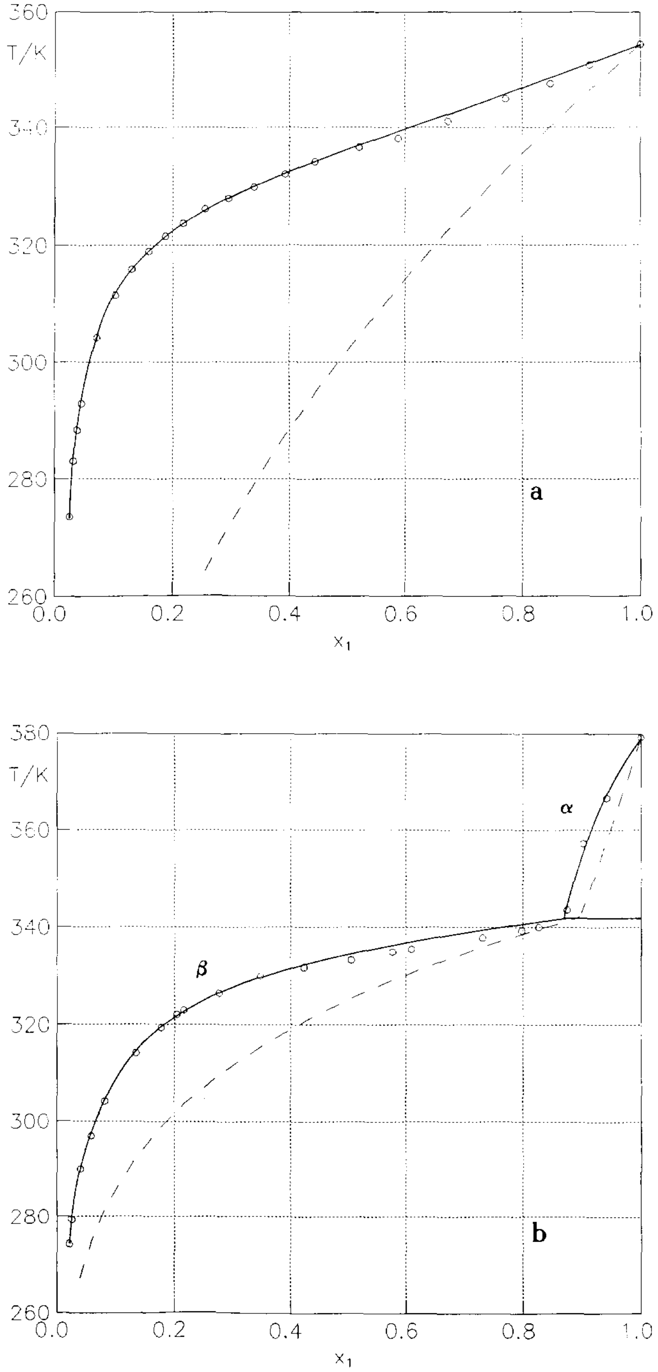
Table 4 (continued)

x_1	T_2/K	T_1/K	γ_1	x_1	T_1/K	γ_1
1-Decanol						
0.0000	280.15			0.1708	340.15	1.624
0.0079	279.85			0.2100	345.05	1.559
0.0104	279.55			0.2479	349.05	1.507
0.0121		279.55	1.827	0.2866	352.35	1.450
0.0142		280.05	1.597	0.3399	356.25	1.383
0.0150		281.85	1.655	0.4304	360.95	1.262
0.0276		295.35	1.712	0.5115	364.85	1.195
0.0500		309.35	1.736	0.5588	366.55	1.150
0.0857		323.35	1.765	0.6168	368.95	1.118
0.1247		332.45	1.698	1.0000	382.15	1.000
1-Dodecanol						
0.0000	297.15			0.2513	349.25	1.496
0.0260	297.05			0.3002	353.25	1.424
0.0336		296.95	1.512	0.3571	357.15	1.354
0.0383		300.35	1.543	0.4082	360.15	1.299
0.0601		313.15	1.688	0.4595	362.85	1.253
0.0891		323.85	1.730	0.5159	365.95	1.224
0.1269		334.35	1.785	0.5570	366.95	1.168
0.1690		340.45	1.658	0.5923	368.55	1.151
0.2117		345.35	1.562	1.0000	382.15	1.000

melting temperature and T is 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) [12,13]

$$-\ln x_1 = \frac{\Delta H_{\mathrm{m}1}}{\mathrm{R}}\left(\frac{1}{T}-\frac{1}{T_{\mathrm{m}1}}\right) - \frac{\Delta C_{\mathrm{pm}1}}{\mathrm{R}}\left[\ln\left(\frac{T}{T_{\mathrm{m}1}}\right)+\frac{T_{\mathrm{m}1}}{T}-1\right] + \frac{\Delta H_{\mathrm{tr}1}}{\mathrm{R}}\left(\frac{1}{T}-\frac{1}{T_{\mathrm{tr}1}}\right) + \ln\gamma_1 \tag{2}$$

where $\Delta H_{\mathrm{tr}1}$ and $T_{\mathrm{tr}1}$ are the enthalpy and the temperature of the solid–solid transition of the solute. The quantitative fit of the solid–liquid equilibrium of Eqs. (1) and (2) has not been tested for the pyrazaboles because sufficiently accurate thermodynamic data are not available, e.g. for $\Delta C_{\mathrm{pm}1}$. Therefore, for the system under investigation, the simplified version of the solubility equations was applied without the $\Delta C_{\mathrm{pm}1}$ term: 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). In this study, only two correlation methods were used to represent the solute activity coefficients (γ_1) from the so-called correlation equations that describe the Gibbs excess energy of mixing (G^{E}): the Wilson equation [14] and the UNIQUAC associated-solution model [15]. Five correlation methods were applied in our first paper [1]: the Wilson, UNIQUAC, NRTL, UNIQUAC


360
T/K
340
320
300
280
260
0.0
0.2
0.4
0.6
0.8
1.0
x_1
a
380
T/K
360
340
320
300
280
260
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0.6
0.8
1.0
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β
b

Fig. 1. (a), (b).

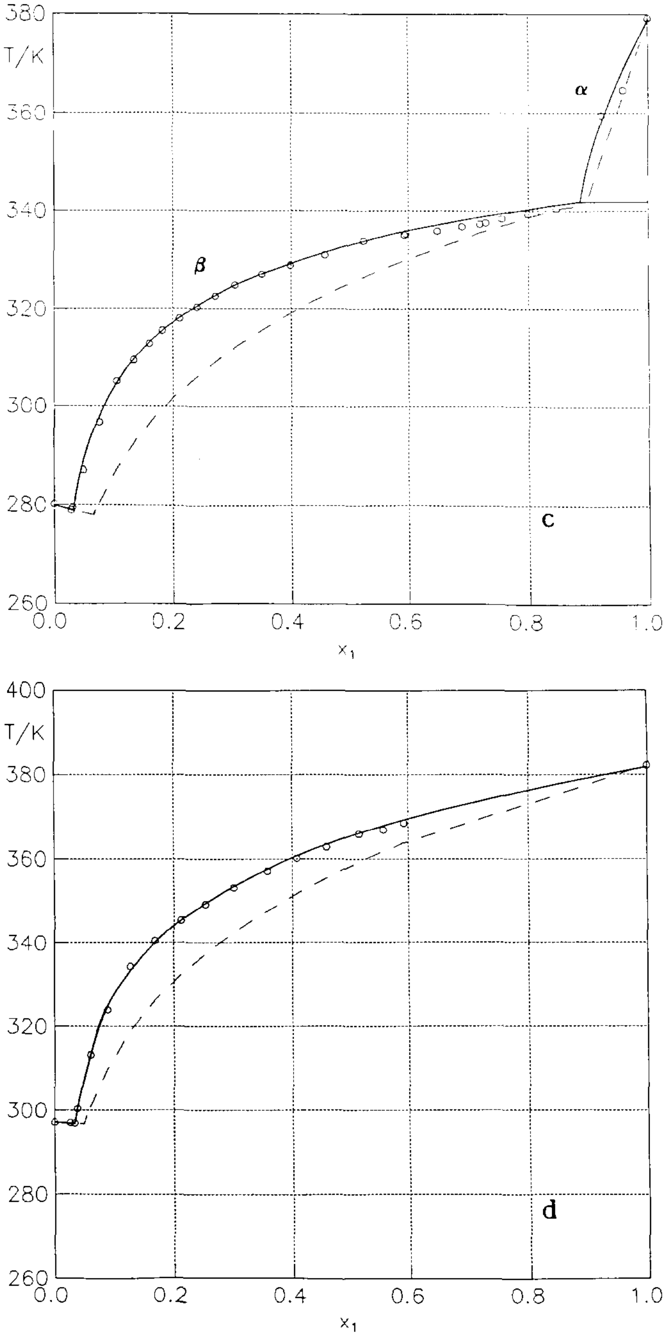

Fig. 1. (a) Solubility of PYR in 1-butanol; (b) solubility of TEP in 1-hexanol; (c) solubility of TEP in 1-decanol; (d) solubility of TPP in 1-dodecanol. The experimental points are fitted to the equations given in the text. The broken line represents the ideal solubility.

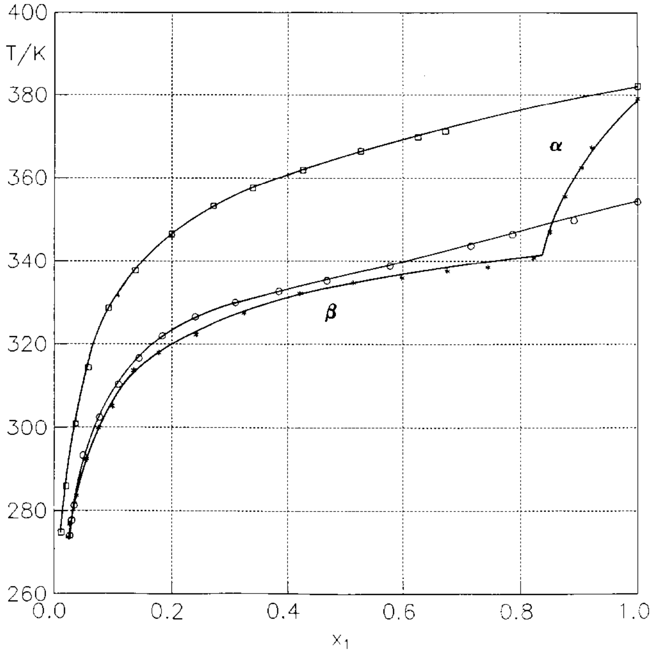

Fig. 2. Solubility of PYR (○), TEP (*) and TPP (□) in 1-dodecanol. Experimental points are matched by curves calculated by UNIQUAC ASM KW equation.

ASM and modified NRTL1 equations; and 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 were presented in a previous paper [16]. The calculations with the UNIQUAC associated-solution model (UNIQUAC ASM) were carried out using a K_2 value as the association constant for n-alkanols at 323.15 K, with the hydrogen-bond formation enthalpy ΔH^0 according to Nagata [10] and presented in Table 5. 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 our previous papers [16,17].

The temperature dependence of the association constant was calculated from the van't Hoff relationship 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 likelihood method for minimization

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

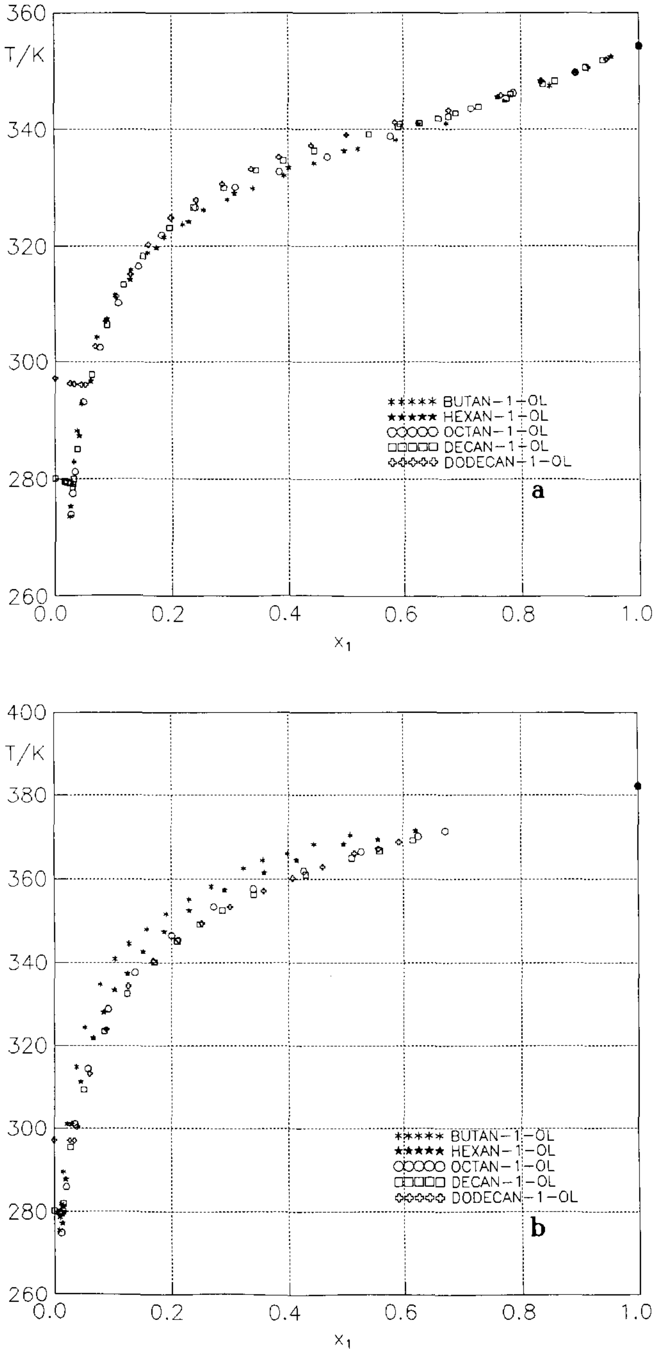

Fig. 3. Solubility of PYR (a) and TPP (b) in 1-butanol (*), 1-hexanol (★), 1-octanol (○), 1-decanol (□) and 1-dodecanol (+).

Table 5
Association parameters of alcohols

Alcohol	K_2 (at 323.15 K)	$-\Delta H^0/(\text{kJ mol}^{-1})$
1-Butanol	83.00	23.30
1-Hexanol	59.60	22.40
1-Octanol	41.20	21.90
1-Decanol	25.30	21.80
1-Dodecanol [a]	14.30	21.80

[a] Values obtained by polynomial extrapolation.

where T_i^{exp} denotes an experimental value of the temperature for a given mole fraction 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 goodness of fit

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

Table 6
Analysis of solubility data of pyrazaboles in five alcohols by the Wilson equation (number of data points in parentheses): values of the parameters and measures of deviations (a in kJ mol^{-1}, σ in K)

Solvent	PYR	TEP	TPP
1-Butanol	(22)	(27)	(20)
$a_{12} \times 10^{-3}$	0.8510	−0.3946	−0.9322
$a_{21} \times 10^{-3}$	1.7688	2.2119	2.7101
σ	1.74	3.01	1.47
1-Hexanol	(16)	(22)	(19)
$a_{12} \times 10^{-3}$	1.0041	−0.3384	−0.9311
$a_{21} \times 10^{-3}$	1.5987	1.6965	2.4703
σ	2.05	2.69	1.00
1-Octanol	(17)	(21)	(14)
$a_{12} \times 10^{-3}$	1.1250	−0.3689	−0.8104
$a_{21} \times 10^{-3}$	1.5177	1.8195	2.0628
σ	1.45	4.78	1.42
1-Decanol	(36)	(34)	(20)
$a_{12} \times 10^{-3}$	1.2564	−0.1572	−0.5706
$a_{21} \times 10^{-3}$	1.4819	1.1957	1.4954
σ	1.11	1.42	0.67
1-Dodecanol	(24)	(25)	(18)
$a_{12} \times 10^{-3}$	1.4628	−0.0053	−0.5773
$a_{21} \times 10^{-3}$	1.3127	0.9604	1.6977
σ	1.35	1.15	1.20

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

Solvent	PYR	TEP	TPP
1-Butanol	(22)	(27)	(20)
Δg_{12}	−1780.37	−1936.26	−953.59
Δg_{21}	3559.44	2824.31	740.69
σ	1.43	2.90	1.82
K_2[a]	39.06	46.18	46.20
Δg_{12}	−1532.02	−1594.10	−1852.79
Δg_{21}	2985.31	2076.88	2417.15
σ	0.50	2.55	0.89
1-Hexanol	(16)	(22)	(19)
Δg_{12}	−1723.49	−2228.93	−665.99
Δg_{21}	3532.84	3710.67	358.09
σ	1.17	3.58	1.60
K_2[a]	55.29	20.64	24.95
Δg_{12}	−1707.28	−1753.94	−1720.51
Δg_{21}	3494.46	2472.28	2143.58
σ	1.21	2.32	0.59
1-Octanol	(17)	(21)	(14)
Δg_{12}	−1654.34	−2017.15	−390.91
Δg_{21}	3465.28	3098.54	76.48
σ	1.43	2.93	2.28
K_2[a]	40.14	42.41	14.38
Δg_{12}	−1649.13	−2027.49	−1648.67
Δg_{21}	3453.69	3125.92	2063.26
σ	1.42	2.90	0.98
1-Decanol	(36)	(34)	(20)
Δg_{12}	−1544.45	−2110.69	902.58
Δg_{21}	3306.33	3443.78	−1011.31
σ	1.78	2.01	1.17
K_2[a]	41.22	7.39	8.49
Δg_{12}	−1649.34	−698.54	−1201.59
Δg_{21}	3531.98	725.72	1336.40
σ	1.72	1.39	0.68
1-Dodecanol	(24)	(25)	(18)
Δg_{12}	−1382.01	−1967.78	−1944.22
Δg_{21}	3012.04	3121.30	2766.59
σ	2.15	2.50	0.92
K_2[a]	68.18	2.77	11.60
Δg_{12}	−1655.11	−611.78	−1773.67
Δg_{21}	3558.74	736.90	2394.93
σ	1.81	1.23	0.88

[a] As an adjustable parameter

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

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

where

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

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

Table 6 lists the results of fitting the solubility curves by the Wilson equation and Table 7 those from UNIQUAC ASM KW equation. For the fifteen systems, the description of the solid–liquid equilibria given by the Wilson equation is within the average r.m.s. deviation of 1.8 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 ($\bar{\sigma} = 2.0$ K). The best solubility correlation in alcohols was obtained with the UNIQUAC ASM KW model, with the association constant as an adjustable parameter. In this case the average r.m.s. deviation is reduced to $\sigma = 1.4$ K.

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