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Solubilities of organoboron compounds in organic solvents.
Part 1. Solid–liquid equilibria of some pyrazaboles + heptane or +2-propanol

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Abstract

Using differential scanning calorimetry, the enthalpies and temperatures of fusion and phase transition have been measured for some pyrazaboles (pyrazabole, 4,4,8,8-tetraethylpyrazabole, and 4,4,8,8-tetrapropylpyrazabole). The solubilities of these pyrazaboles in heptane and 2-propanol have been determined at temperatures ranging from the melting point of the solute to 273 K. Five correlation methods were applied: the Wilson, UNIQUAC, NRTL, UNIQUAC ASM and modified NRTL1 equations.

The r.m.s. deviations of the solubility temperatures for all measured data vary from 2 to 7 K and depend on the particular equation used. The best solubility correlation in heptane was obtained with the Wilson equation and in alcohol with the UNIQUAC ASM KW or NRTL1 KW equations, with the association constants as adjustable parameters. In the calculations, the existence of one solid–solid first-order phase transition in tetraethylpyrazabole has also been taken into consideration.

LIST OF SYMBOLS

a_{12}	binary interaction parameter of the Wilson equation
ΔC_p	difference between the 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
ΔH_{m1}	molar enthalpy of fusion of the 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

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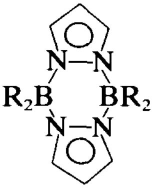
R	universal gas constant
T^{exp}	experimental equilibrium temperature
T^{cal}	calculated equilibrium temperature
T_{m1}	melting point temperature of the pure solute
T_{tr1}	temperature of transition point
V_1, V_2	molar volume of the solute, solvent
x_1	molar fraction of the solute

Greek letters

α_{12}	non-randomness constant of NRTL equations
γ_1	activity coefficient of the 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

INTRODUCTION

Over the last ten years, there has been a large increase in the number of papers dealing with solid–liquid equilibria in new organic systems. This interest is due to the trend in the petroleum industry towards heavier feedstocks and in organic syntheses in which a substantial database of thermodynamic properties has to be developed for systems containing both normal and heavier (also organometallic) components in substantial quantities. The enthalpies of fusion and phase transition, and the activity coefficient data, which are needed for many design calculations, are not published for systems containing organoboron compounds. This is the first publication to report the solubilities of such systems. We have chosen to investigate pyrazaboles, in which the existence of boron in a four-coordinate environment and the presence of the heteroaromatic system produce the high chemical stability of these compounds [1].



where R is H, Et, n-Pr.

Most pyrazaboles are unaffected by air or water; they are stable towards aqueous alkalis but slowly decompose in boiling hydrochloric acid.

The first X-ray crystallographic and molecular structure study of a pyrazabole was reported for the species H(pz′)B(pz′)$_2$BH(pz′) (where pz′

is 3,5-dimethylpyrazolyl) [2]. The compound was found to exist in a chair conformation of the central B_2N_4 ring with the two terminal pyrazolyl groups in the trans arrangement. Later, pyrazaboles were found to exist in either boat, chair or planar conformation of the B_2N_4 ring and no steric influence of the terminal substituents was confirmed [3]. Rather, the individual structures of pyrazaboles seem to result from crystal packing effects. The simple pyrazabole (PYR), where R is H, exists in a boat conformation of the central B_2N_4 ring [4].

The aim of this work was to study the solubility of selected pyrazaboles, and to attempt a correlation of all the experimental results with established theories of solutions.

EXPERIMENTAL

Materials

Pyrazabole (PYR), tetraethylpyrazabole (4,4,8,8-tetraethylpyrazabole) (TEP) and tetrapropylpyrazabole (4,4,8,8-tetrapropylpyrazabole) (TPP) were synthesized according to ref. 1. The solvents, heptane (VEB Jena Pharm., Germany, $n_D^{298.15} = 1.38520$) and 2-propanol (POCH, Gliwice, Poland, $n_D^{298.15} = 1.3750$), were dried over 4A molecular sieves (BDH, Poole, UK) and fractionally distilled through a 50-plate laboratory column.

The characteristics of the solutes and solvents are listed in Table 1.

TABLE 1

Characteristics of the solutes and solvents

Compound	$V_m^{\ominus}$ [a]/ cm^3 mol^{-1}	T_{m1}/K	ΔH_{m1}/ kJ mol^{-1}	T_{tr1}/K	ΔH_{tr1}/ kJ mol^{-1}
PYR	170.0	354.25 [b]	11.83		
TEP	287.0	379.15 [c]	3.22	342.30 ± 0.15	28.61
TPP	345.0	382.15	33.00		
Heptane	147.4 [d]				
2-Propanol	76.8 [d]				

[a] $V_m^{\ominus}$ is the molar volume at 298.15 K. [b] $T_{m1} = 353.15–354.15$ K [5]. [c] $T_{m1} = 379.15–380.15$ K [5]. [d] Data from ref. 6.

Measurements

The fusion and transition enthalpies were measured using a heat-flux DSC, a Unipan model 605M, interfaced to an IBM-AT computer. Calibration was made using the melting points of gallium, indium, cadmium, lead, tin, zinc, naphthalene and benzoic acid. The metals were 99.999% grade and the organic compounds were above 99.95% purity. The temperature calibration was made using the melting temperature of the calibrants as determined by cryometric analysis. Experiments were carried out at a scan rate of 2 K min^{-1}.

The solubilities were determined by a dynamic (synthetic) method. Mixtures of solute and solvent, prepared by weighing pure components to within 50 μg, were heated very slowly (at <2 K h^{-1} close to the equilibrium temperature) with continuous stirring, inside a Pyrex glass cell placed in a thermostat. The temperatures at which the crystals disappeared, detected visually, were measured with a calibrated Anschutz thermometer (TGL 11986, H. Schlegel, Ilmenau, Germany), subdivided in 0.1 K divisions, that was totally immersed in the thermostating liquid. The accuracy of the temperature measurements was ±0.1 K.

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.

TABLE 2

Experimental mole fraction solubilities and activity coefficients of PYR

x_1	T_1/K	γ_1	x_1	T_1/K	γ_1
Heptane					
0.0129	274.35	24.066	0.2902	332.25	2.641
0.0175	283.35	20.916	0.3240	333.35	2.399
0.0283	290.85	14.722	0.3671	334.55	2.150
0.0349	295.85	12.967	0.4181	335.75	1.917
0.0446	301.55	11.121	0.4576	336.45	1.767
0.0559	305.75	9.460	0.5032	337.55	1.629
0.0685	309.75	8.198	0.5625	338.85	1.481
0.0868	315.15	6.999	0.6072	340.05	1.392
0.1084	319.55	5.964	0.6918	343.05	1.268
0.1325	322.75	5.100	0.7596	345.75	1.193
0.1611	325.35	4.345	0.8433	349.05	1.117
0.1948	327.75	3.710	0.8894	350.45	1.076
0.2310	329.95	3.220	0.9338	351.95	1.043
0.2529	330.75	2.972	1.0000	354.25	1.000
2-Propanol					
0.0118	273.95	26.110	0.3323	329.85	2.236
0.0219	290.05	18.770	0.3733	331.65	2.037
0.0378	296.15	12.031	0.4304	334.65	1.836
0.0578	304.85	9.024	0.4807	335.65	1.665
0.0919	313.15	6.423	0.5487	338.05	1.503
0.1282	317.75	4.917	0.6162	340.95	1.387
0.1595	320.45	4.104	0.6919	343.95	1.281
0.1912	323.15	3.553	0.7446	346.15	1.222
0.2217	324.85	3.136	0.8187	348.65	1.145
0.2562	326.85	2.787	0.8993	351.45	1.077
0.2921	328.15	2.487	1.0000	354.25	1.000

TABLE 3

Experimental mole fraction solubilities and activity coefficients of TEP

x_1	$T_{\beta 1}$/K	γ_1	x_1	$T_{\beta 1}$/K	$T_{\alpha 1}$/K	γ_1
Heptane						
0.0404	272.95	1.299	0.5953	329.95		0.995
0.0544	278.55	1.279	0.6790	333.45		0.985
0.1057	291.45	1.209	0.7233	335.45		0.990
0.1619	300.25	1.160	0.7676	337.25		0.991
0.2262	307.65	1.128	0.8101	338.65		0.984
0.3001	313.15	1.058	0.8510	339.75		0.972
0.3715	318.05	1.032	0.8927		346.65	1.018
0.4479	322.35	1.005	0.9374		366.65	1.030
0.5299	326.55	0.990	1.0000		379.15	1.000
2-Propanol						
0.0097	274.55	5.820	0.4383	333.35		1.507
0.0116	279.45	6.215	0.5024	334.65		1.375
0.0194	291.35	6.503	0.5728	336.15		1.269
0.0293	299.15	6.065	0.6863	339.05		1.167
0.0416	305.05	5.472	0.7694	341.95		1.146
0.0551	309.65	4.978	0.8250		346.95	1.102
0.1166	319.95	3.502	0.8909		366.65	1.084
0.1731	324.75	2.815	0.9122		371.35	1.073
0.2589	328.35	2.142	1.0000		379.15	1.000
0.3379	330.65	1.780				

RESULTS AND DISCUSSION

Fusion and solid–solid transitions data are listed in Table 1 and Fig. 1 shows a DSC curve for TEP.

Substitution of ethyl and propyl groups in positions 4 and 8 of pyrazabole results not only in an increase in molecular weight ($M_{\mathrm{PYR}} = 159.8\ \mathrm{g\ mol^{-1}}$, $M_{\mathrm{TEP}} = 272.0\ \mathrm{g\ mol^{-1}}$ and $M_{\mathrm{TPP}} = 328.1\ \mathrm{g\ mol^{-1}}$) but also in an increase in the melting temperatures and fusion enthalpies, taking into account the effects of fusion and phase transition for TEP. The phase transition is accompanied by a relatively high enthalpy of transformation, $\Delta H_{\mathrm{tr1}} = 28.61\ \mathrm{kJ\ mol^{-1}}$, which suggests a boat–chair conformational change. According to ref. 4, pyrazabole exists in a boat conformation. It can also be assumed that the high-temperature form of TPP and TEP exists as the boat conformation, based on the molecular structure data of similar systems, e.g. tetrakis(methylthio)pyrazabole [3].

The solubility of PYR in both solvents 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

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
Heptane					
0.0332	273.95	0.498	0.3185	339.95	0.865
0.0338	275.75	0.538	0.3376	347.55	1.053
0.0606	288.25	0.560	0.4395	354.95	1.026
0.0841	296.15	0.582	0.5097	361.55	1.085
0.1113	303.25	0.602	0.5426	364.35	1.109
0.1428	311.45	0.663	0.5919	367.85	1.128
0.1783	318.45	0.702	0.6511	371.05	1.125
0.2120	324.05	0.739	1.0000	382.15	1.000
0.2430	329.15	0.773			
2-Propanol					
0.0041	274.95	4.252	0.0977	343.25	3.165
0.0045	278.25	4.597	0.1292	347.25	2.725
0.0058	283.65	4.680	0.1528	350.35	2.549
0.0073	289.65	4.968	0.1830	353.15	2.549
0.0091	296.15	5.384	0.2194	357.05	2.329
0.0150	305.95	5.017	0.2551	359.85	2.196
0.0291	319.35	4.457	0.3036	364.25	2.059
0.0404	326.45	4.207	0.3799	369.75	1.977
0.0493	330.35	3.980	0.3928	371.25	1.858
0.0605	334.05	3.705	1.0000	382.15	1.000
0.0785	339.05	3.402			

ideal values in heptane ($\gamma_1 \approx 1$) and are lower than the ideal values in 2-propanol ($\gamma > 1$). TEP has the highest solubility in both solvents because of the solid–solid phase transition below the melting point. 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 in Fig. 2a–f.

The structure of boron heterocycles contains positive charges delocalized on the pyrazole 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 and an increase in the intermolecular solute–solvent association are expected on passing from inert heptane to active hydroxylic solvent. However, the above observations are not confirmed by the results of the solubility measurements. The solubilities of PYR, TEP and TPP in alcohol are close to or much lower than those in heptane (see Fig. 2a–f). It may be concluded that the solids under study are not able to form intermolecular hydrogen bonds or stable complexes in solution with polar solvents.

The present work is a continuation of systematic studies on solid–liquid

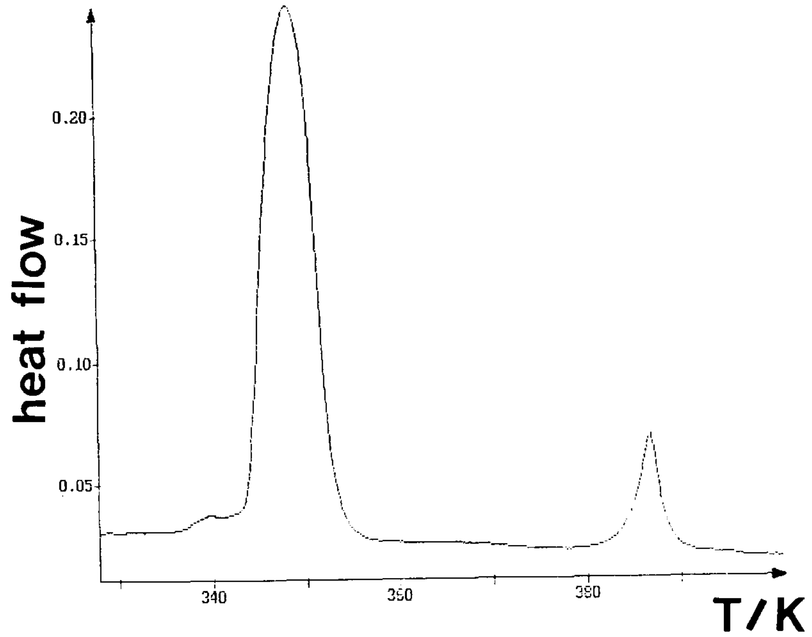


Fig. 1. DSC diagram of TEP.

equilibria in binary and ternary systems and on defining methods of correlation or prediction of the solute activity coefficients γ_1 and solubility T_1^{cal}.

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

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

where x_1 is the mole fraction, γ_1 the activity coefficient, ΔH_{m1} the enthalpy of fusion, $\Delta C_{p\mathrm{m1}}$ the solute heat capacity during the melting process, and T_{m1} the melting temperature and T the equilibrium temperature, of the solute respectively. If the solid–solid transition occurs before fusion, an additional term must be added to the right-hand side of eqn. (1) [7, 8]

$$\begin{aligned}-\ln x_1 = {}& \frac{\Delta H_{\mathrm{m1}}}{R}\left(\frac{1}{T}-\frac{1}{T_{\mathrm{m1}}}\right) - \frac{\Delta C_{p\mathrm{m1}}}{R}\left[\ln\left(\frac{T}{T_{\mathrm{m1}}}\right)+\frac{T_{\mathrm{m1}}}{T}-1\right]\\ &+\frac{\Delta H_{\mathrm{tr1}}}{R}\left(\frac{1}{T}-\frac{1}{T_{\mathrm{tr1}}}\right)+\ln\gamma_1\end{aligned} \tag{2}$$

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 eqns. (1) and (2) has not been tested for the pyrazaboles, because

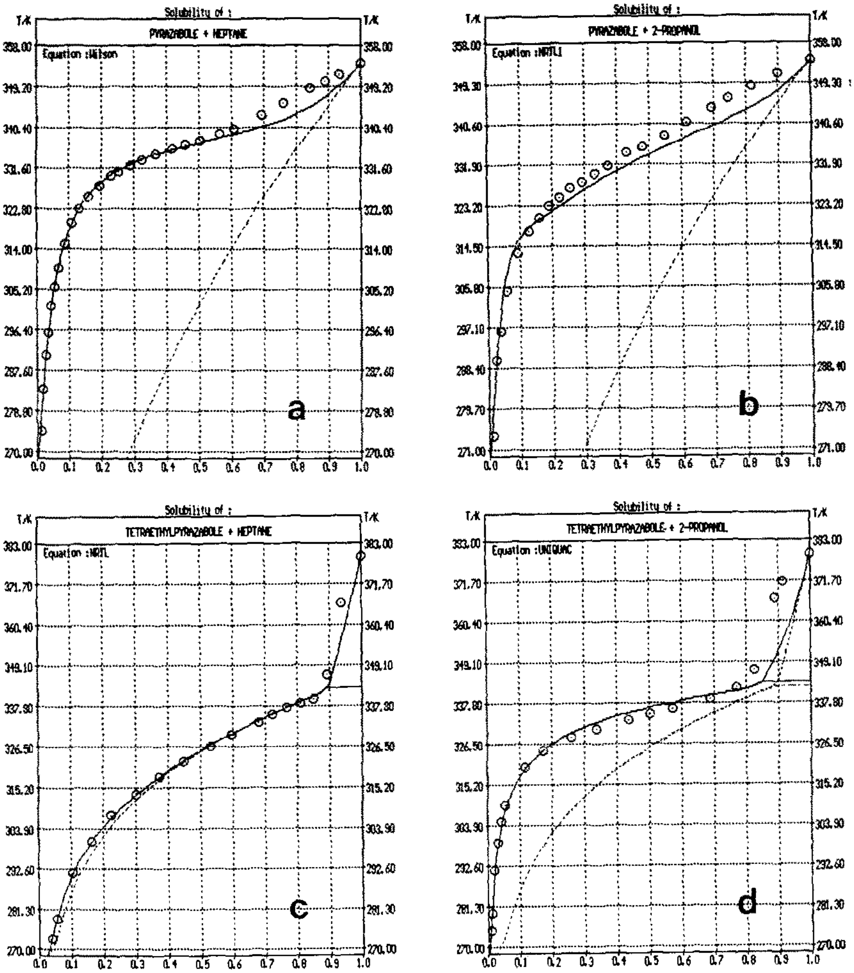


Fig. 2. (a) Solubility of PYR in heptane. (b) Solubility of PYR in 2-propanol. (c) Solubility of TEP in heptane. (d) Solubility of TEP in 2-propanol. (e) Solubility of TPP in heptane. (f) Solubility of TPP in 2-propanol. The experimental points are fitted to the equations given in the text. The dotted line represents the ideal solubility.

sufficiently accurate thermodynamic data are not available, e.g. for ΔC_{pm1}. Therefore, for the systems under investigation the simplified version of the solubility equations was applied without the ΔC_{pm1} term: eqn. (1) for temperatures above the temperature of transition and eqn. (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, five methods were used to represent the solute activity coefficients (γ_1) from the so-called correlation equations that describe the Gibbs excess free energy of mixing (G^E): the Wilson equation [9], the simple UNIQUAC equation of Abrams and Prausnitz [10], the UNIQUAC associated-solution model [11] and two NRTL equations [12, 13].

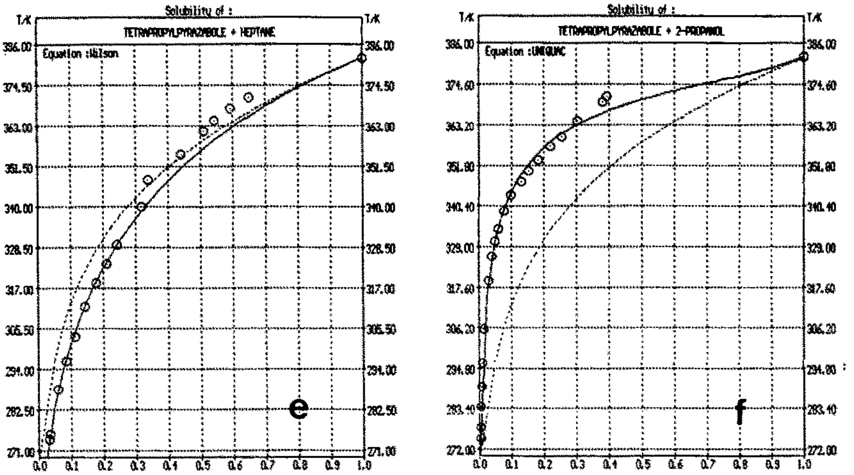


Fig. 2. (continued)

The exact mathematical forms of the equations were presented in a previous paper [14]. The calculations with the UNIQUAC associated-solution model (UNIQUAC ASM) and NRTL1 were carried out using a K_2 value of 70.00 as the association constant for 2-propanol at 298.15 K, with the hydrogen-bond formation enthalpy $\Delta H^{\ominus}$ being −22.00 kJ mol^{-1}. In addition, calculations with K_2 as the third adjustable parameter were made using the same value of $\Delta H^{\ominus}$. Moreover, the results were correlated using two models of association, those of Mecke–Kempter (MK) and of Kretschmer–Wiebe (UNIQUAC ASM KW). The pure component structural parameters r (volume parameter) and q (surface parameter) were obtained according to our previous papers [14, 15].

The temperature dependence of the association constants 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 Marquardt's maximum neighbourhood method for minimization [16]

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

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 (eqn. (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 eqn. (4) was used as a measure of the solubility correlation

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

where T_i^{exp} and T_i^{cal} are, respectively, the experimental and calculated temperatures of the ith point, 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

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

where V_1 and 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 1 and 2 components, and a_{12} is the binary interaction parameter.

Tables 5 and 6 list the results of fitting the solubility curves by the five equations tested with the two models of association. For the six systems presented in Table 5, the best descriptions of the solid–liquid equilibria are given by the Wilson equation. Taking into consideration the association of 2-propanol in the form of the UNIQUAC ASM and NRTL1 equations, a better mathematical description is observed for all the systems. The Kretschmer–

TABLE 5

Analyses of the solubility data of pyrazaboles in heptane and 2-propanol by the Wilson, UNIQUAC and NRTL equations (number of data points in parentheses): values of the parameters and measures of deviations (a in kJ mol^{-1}; Δg in J mol^{-1}; σ in K)

Model and parameters	PYR		TEP		TPP	
	Heptane (28)	2-Propanol (22)	Heptane (18)	2-Propanol (19)	Heptane (17)	2-Propanol (21)
Wilson						
$a_{12} \times 10^{-3}$	1.5266	1.1572	−0.0471	−0.1314	0.2717	−0.5405
$a_{21} \times 10^{-3}$	1.4777	1.7264	0.2615	1.9324	−0.1651	2.3659
σ	1.62	3.76	2.78	7.43	3.43	2.32
UNIQUAC						
Δg_{12}	−167.87	1575.88	−40.26	3184.31	−1051.11	3567.66
Δg_{21}	1961.9	872.84	228.58	−655.90	1234.12	−874.81
σ	5.49	7.43	2.78	7.88	3.34	2.95
NRTL						
Δg_{12}	1654.49	1120.65	−2378.81	1447.44	−3225.84	3311.71
Δg_{21}	5877.00	6403.65	4051.63	3350.54	3202.35	1639.04
σ	5.14	7.04	2.78	7.55	3.43	2.19

TABLE 6

Analyses of the solubility data of pyrazaboles in 2-propanol by means of the UNIQUAC ASM (KW or MK) and NRTL1 (KW or MK) equations (number of data points in parentheses): values of parameters and measures of deviations (Δg in J mol^{-1}; σ in K)

Model and parameter	PYR (22)	TEP (19)	TPP (21)
UNIQUAC ASM KW			
Δg_{12}	−1658.72	−1639.10	−1557.10
Δg_{21}	3463.47	2317.44	1997.62
σ	2.75	5.97	2.47
K_2[b]	147.72	246.94	141.54
Δg_{12}	−1901.97	−2180.75	−2336.32
Δg_{21}	4056.66	3602.79	3836.47
σ	2.19	4.73	1.76
UNIQUAC ASM MK			
Δg_{12}	−1859.02	−1971.52	−1259.87
Δg_{21}	3896.89	3009.78	1376.49
σ	3.00	6.77	2.75
K_2[b]	120.08	252.15	101.64
Δg_{12}	−2031.14	−2347.36	−2417.52
Δg_{21}	4374.99	4066.35	4033.39
σ	2.45	5.61	2.69
NRTL1 KW[a]			
Δg_{12}	−1039.28	−477.55	−469.91
Δg_{21}	6171.65	1179.56	605.25
σ	2.71	6.03	3.32
K_2[b]	203.86	280.59	220.45
Δg_{12}	−1441.57	−1488.66	−1337.33
Δg_{21}	7632.61	5475.23	4412.16
σ	1.84	4.61	1.83
NRTL1 MK[a]			
Δg_{12}	−1281.48	−965.72	−655.87
Δg_{21}	6655.00	2713.85	825.28
σ	2.99	6.82	3.30
K_2[b]	162.76	290.55	181.36
Δg_{12}	−1611.38	−1718.37	−1589.07
Δg_{21}	7787.43	6484.60	5567.88
σ	1.95	5.32	1.85

[a] Parameter $\alpha_{12} = 0.3$. [b] With K_2 as an adjustable parameter.

Wiebe model of association gives better correlation results. In this case the r.m.s. deviations are reduced to $\sigma = 1.8$–4.6 K for both theories of solution, UNIQUAC ASM and NRTL1, and they are comparable with each other.

In general, the UNIQUAC ASM and NRTL1 equations with three adjustable parameters also give results of the same order for all the systems, being especially bad for the system TEP + 2-propanol. The results of the solid solubility correlation, obtained using the simple two-parameter equations of Redlich–Kister and van Laar, are not acceptable (not published).

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