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Competition Among Aromatic Guests for the Host Tetrakis(4-methylpyridine)nickel(II) Isothiocyanate and a Basis for the Observed Selectivity*

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Abstract. In continuing attempts to determine the basis for the selectivity shown by the host $Ni(4\text{-mepy})_4(NCS)_2$ (**1**) toward aromatic guests, distribution data between solid and liquid phases are reported for seven ternary systems at room temperature. These consist of **1**, *p*-xylene, and each of the following: *p*-bromotoluene, *p*-chlorotoluene, *p*-fluorotoluene, *p*-dichlorobenzene, benzene, and 4-methylpyridine, as well as the system **1**–*p*-chlorotoluene–*p*-dichlorobenzene. The results, as well as those for five systems already published, have been reviewed and a hierarchy of selectivity developed. After correcting the observed selectivity for inequality of guest vapour pressures the order of decreasing preference is found to be *p*-bromotoluene > *p*-dichlorobenzene > *p*-chlorotoluene > deuterated and protiated *p*-xylenes > ethylbenzene > 4-methylpyridine > *p*-fluorotoluene > toluene > benzene. With the exception of 4-methylpyridine, this is the same as the order of decreasing van der Waals length of the guest molecule and, where known, the order of enthalpy of inclusion. Although longer guest molecules and those with higher vapour pressures are favoured in selectivity, guests with longer molecules are likely to have lower vapour pressures. The activity coefficients of the included guests are calculated assuming that the liquid phases follow Raoult's law.

Key words: Selectivity of guests, $Ni(4\text{-mepy})_4(NCS)_2$, van der Waals length.

1. Introduction

The ability of tetrakis(4-methylpyridine)nickel(II) isothiocyanate (**1**) to include a wide variety of guests, particularly aromatic ones, was first noted by Schaeffer and co-workers [1], who demonstrated that the inclusion could be used for fractionation of mixtures. For example, if a solution of three selected aromatic liquids be stirred with **1** the resulting solid contains these aromatics in a proportion which differs from that in the original solution. Subsequently, in order to approach the subject in a more fundamental manner, Smith and co-workers showed [2, 3] that **1** forms 1 : 1 inclusion compounds with such guests as *p*-xylene, *p*-dichlorobenzene, ethylbenzene, 4-methylpyridine (4-mepy) and toluene, and presented distribution data determined when **1** is equilibrated with only two guests at a time. In particular, it was shown that there appears to be a linear relation (within experimental error) between $\ln R_L$ and $\ln R_S$, where R_L is the mole ratio of the two guests in the liquid phase and R_S the mole ratio in the coexisting solid phase. However, the parameters of the linear relation depend strongly upon

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the guests used. The guest pairs first studied from this point of view [3] were *p*-xylene–ethylbenzene, *p*-xylene–toluene, *p*-xylene–*p*-dichlorobenzene and ethylbenzene–toluene. Since that time distribution studies with other pairs, including those differing only isotopically [4–6] have been conducted using the same host in order to expand the number of guests significantly in the hope of determining some generally applicable principle underlying the selectivity process. This, in turn, should be useful in predicting feasible separations.

Presented below are (1) the unpublished data on six new guest pairs, (2) a revision of the data for the *p*-xylene–*p*-dichlorobenzene pair, (3) an analysis of all the results revealing an underlying principle which seems to determine selectivities.

The experiments here reported are really phase studies in the ternary system **1**–Guest A(1)–Guest B(1) at 1 atm and room temperature. Exceptions to this are the two isotopic guest pairs [4, 6] where pentane was used as cosolvent, and systems in which one of the guests, *p*-dichlorobenzene, is a solid. Of interest are the equilibria between liquid solutions and solid solutions, with the simplifications that, with two exceptions, the liquid phase contains no host and the solid phase contains only the 1:1 inclusion compound of A and the 1:1 inclusion compound of B, the latter two being isomorphous. Figure 1, plotted in mole per cent, shows a common situation schematically, which is not unlike some earlier ionic system studies with water [7]. In this event all the experimentally determined tie lines crossing the trapezoidal area pass on the one side of the host apex when produced upward as drawn. This means that $R_S > R_L$ where R is the mole ratio of B to A, and B would be described as selectively included over A for all proportions of A and B. There are, however, other conceivable dispositions of the tie lines giving rise to several types of distribution behaviour as noted by Bakhius Roozeboom [8]. For example, the tie lines on the left in Figure 1 might very well pass to the right of the apex when produced, but those on the right pass to the left. This would represent

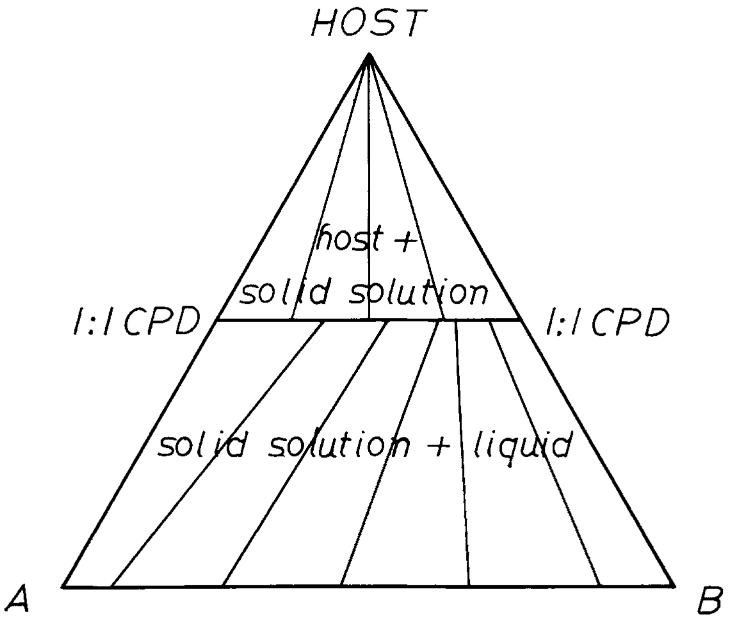

Fig. 1. Typical isotherm (schematic) for a system of two guests competing for the same host.

a reversal of selectivity as the overall proportions of A and B are altered. This possibility, illustrated below, emphasizes the importance of investigating selectivities over a range of A/B ratios.

2. Experimental

The host (**1**) was prepared as described elsewhere [9]. Gravimetric nickel determinations by precipitation with dimethylglyoxime gave results agreeing with the calculated value (10.73% Ni) within 0.2%. That **1** forms 1:1 inclusion compounds with the guests originally studied had already been established [2, 3], and this was also found to be true for the newly reported ones. They were made, as usual, by stirring a suspension of 2.0 g host in 10 ml of a solution of liquid guest containing 0.5 ml 4-mepy for a day or two, filtering off the resulting solid, and air drying to (nearly) constant weight. (For benzene as guest the 4-mepy was omitted.) Gravimetric nickel analysis of the products, a quite accurate technique, gave the following results confirming the 1:1 stoichiometry: % Ni calc. for 1:1, % Ni found: 8.93, 8.99; 8.71, 8.65; 8.17, 8.17; 9.39, 9.40; 9.17, 9.03 for *p*-fluorotoluene, *p*–chlorotoluene, *p*-bromotoluene, benzene, and 4-mepy, respectively. It is to be noted that 4-mepy in the last mentioned is playing a dual role as included guest and ligand for the host. Moreover, although 4-mepy forms a 1:1 inclusion compound with **1** when other potential guests are absent, it does not appear to be so included when they are present as long as only moderate quantities of it are used. It is, in fact, commonly added in small amounts as above, in the preparation of inclusion compounds of other guests.

The distribution equilibria when two guests are present simultaneously were determined following the same general procedures as in the earlier work [3]. Excess of a solution of one guest in the other was mixed with host, placed in a sealed Pyrex tube and tumbled on a wheel at room temperature for a period of at least several weeks. Thermostatting of these mixtures at 25 °C, adopted earlier, was discarded, as it was felt that errors introduced thereby would be smaller than those from other sources, such as slowness of equilibration. The liquid and solid phases were then separated and the latter air dried. The liquids were diluted with pentane and (usually) subjected to gas chromatography after calibration of the method. The solids, with one exception, were dissolved in dilute HCl, the guests extracted with pentane and treated similarly. (With the pair *p*-xylene–4-mepy the latter was determined by addition of excess standard 1N H_2SO_4 and back titration with standard 1N NaOH using a pH meter. Addition of excess acid converts the 4-mepy into its sulphate, and careful titration with base shows two endpoints marking the beginning and end of the reconversion to the free amine.)

3. Results and Discussion

In Table I are presented the data for six guest pairs not previously reported, and revised data for the pair *p*-xylene–*p*-dichlorobenzene after a reconsideration of the results reported earlier [3] and the addition of new data. All of these results are plotted as $\ln R_S$ against $\ln R_L$ in Figures 2(a) and (b).

In the first place it may be noticed that, in the range of R values covered – and only feasible ranges were studied – R_S changes continuously with R_L, so that there are no invariant liquids and the 1:1 inclusion compounds of the guests of each pair form a continuous series of solid solutions. Allowing for larger experimental error for the more extreme values of R it appears, as before [3], that the distributions are fairly represented by a linear relation between $\ln R_S$ and $\ln R_L$. Fitting the data by least-squares to the equation

$$\ln R_S = m \ln R_L + b \tag{1}$$

Table I. Guest distribution (mole ratios) with the host $Ni(4\text{-mepy})_4(NCS)_2$ at room temperature

R_L	R_S	R_L	R_S
p-xylene/*p*-chlorotoluene		*p*-xylene/*p*-dichlorobenzene	
0.244	0.245	0.914	1.03
0.323	0.330	0.955	1.01
0.335	0.337	0.987	1.26
0.376	0.374	0.988	1.23
0.497	0.502	3.90	3.93
0.965	0.976	3.94	4.72
1.97	1.99	3.95	4.46
2.73	2.70	4.00	3.88
2.82	2.86	5.92	6.63
2.94	2.95	5.94	6.31
4.08	4.10	*p*-xylene/*p*-fluorotoluene	
p-xylene/*p*-bromotoluene		0.345	1.40
0.642	0.610	0.378	1.44
1.08	1.07	0.506	1.68
1.09	1.06	0.506	1.76
1.99	1.97	1.02	2.62
4.08	3.90	1.09	2.75
4.08	3.92	1.89	4.14
p-dichlorobenzene/*p*-chlorotoluene		2.10[a]	5.10[a]
0.195	0.200	2.70	5.01
0.246	0.250	2.46	4.95
0.328	0.328	*p*-xylene/4-methylpyridine	
0.333	0.340	0.033	0.518
0.387	0.399	0.053	1.00
0.477	0.501	0.103	2.08
0.787	0.800	0.119	1.69
0.828[a]	0.940[a]	0.200	1.93
0.999	1.02	0.206	2.19
p-xylene/benzene		0.239	4.20
0.096	6.06	0.270	3.50
0.191	7.57	0.281	2.25
0.381	9.43	0.509	5.59
0.640	11.54	0.657	3.78
0.943	12.41	1.41	13.3

[a] Excluded from least-squares treatment.

gives the values of m and b presented in Table II. It should be noted that in general $m \neq 1$, except for isotopic guest pairs [4, 6, 10]. It follows that R_S/R_L, a commonly used quantitative description of selectivity, or separation factor, is not generally a constant for a given system. Accordingly, in order to describe the selectivity in a particular system the value of R_S/R_L for R_S equal to unity has been chosen. This is considered a reasonable, if somewhat arbitrary, means of comparing the behaviour of the various systems. These quantities are therefore also tabulated, and the systems listed in the order of their increasing value. (For $R_S = 1$, $R_S/R_L = e^{b/m}$.) As *p*-xylene is in the numerator of all but two of the pairs, the values of R_S/R_L suggest the selectivities of those guests in the denominator relative to each other. Thus the guests may be arranged in the order of preference vis-à-vis *p*-xylene: *p*-xylene-d_6 >

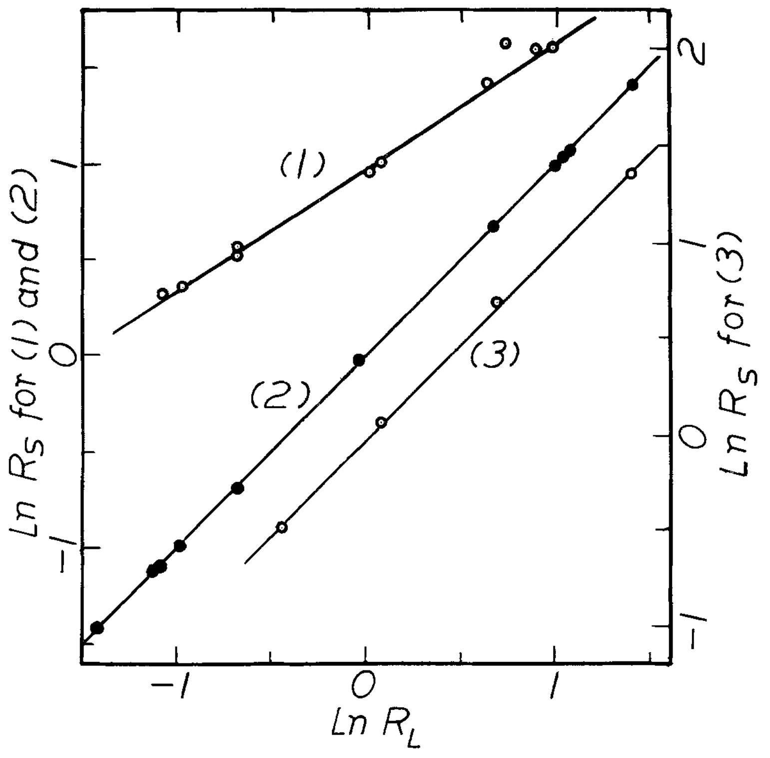

Fig. 2(a). Distribution of guests between liquid and solid phases: (1) *p*-xylene/*p*-fluorotoluene (○); (2) *p*-xylene/*p*-chlorotoluene (●); (3) *p*-xylene/*p*-bromotoluene (○).

Table II. Parameters for $\ln R_S = m \ln R_L + b$

Guest pair	m	b	R_S/R_L ($R_S = 1$)
p-xylene/*p*-xylene-d_6	0.97[a]	−0.12	0.88
p-xylene/*p*-xylene-d_{10}	0.97[a]	−0.09	0.91
p-xylene/*p*-bromotoluene	1.00	−0.03	0.97
p-xylene/*p*-xylene	1.00	0	1.00
p-xylene/*p*-chlorotoluene	0.999	0.007	1.01
p-dichlorobenzene/*p*-chlorotoluene	1.00	0.02	1.02
p-xylene/*p*-dichlorobenzene	0.95	0.15	1.18
p-xylene/*p*-fluorotoluene	0.64	0.99	4.63
ethylbenzene/toluene	0.60	0.94	4.75
p-xylene/ethylbenzene	1.16	2.3	7.56
p-xylene/toluene	0.64	1.72	14.4
p-xylene/4-methylpyridine	0.75	2.1	16.5
p-xylene/benzene	0.32	2.56	2790

[a] These slopes were assumed to be unity in Refs. [6] and [10] because they are practically so within experimental error, ±0.02. Treatment of the data by the methods used for the other systems, however, yields the values given above.

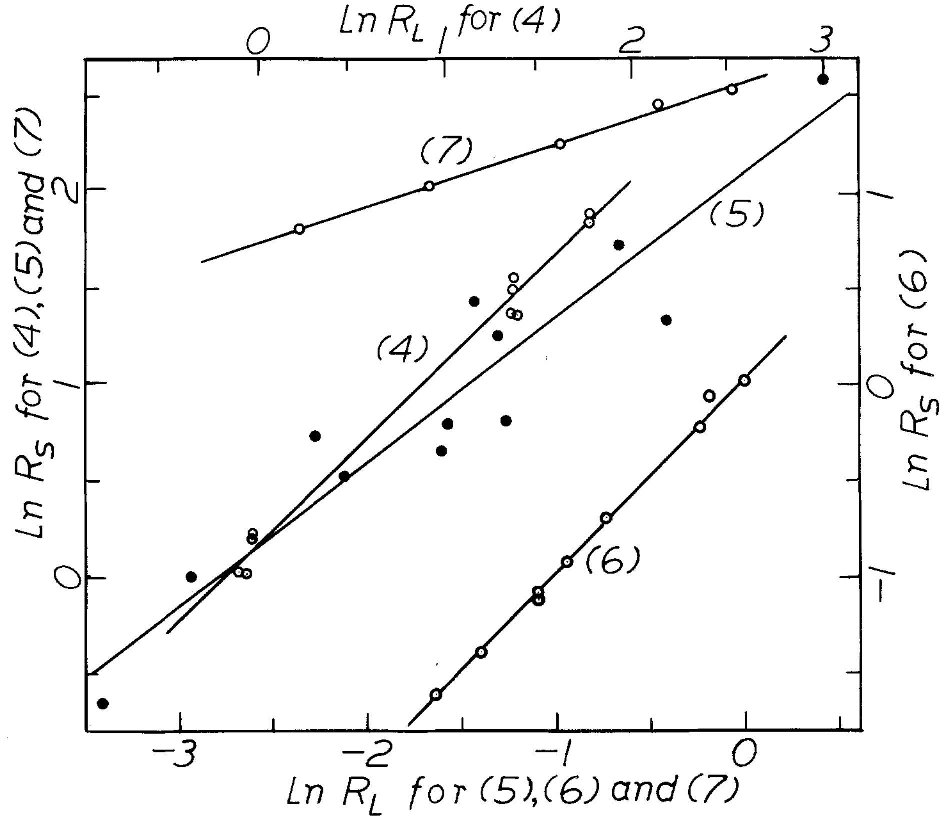

Fig. 2(b). Distribution of guests between liquid and solid phases: (4) *p*-xylene/*p*-dichlorobenzene (○); (5) *p*-xylene/4-methylpyridine (●); (6) *p*-dichlorobenzene/*p*-chlorotoluene (○); (7) *p*-xylene/benzene (○).

p-xylene-d_{10} > *p*-bromotoluene > *p*-xylene > *p*-chlorotoluene > *p*-dichlorobenzene > *p*-fluorotoluene > ethylbenzene > toluene > 4-mepy > benzene.

The guest pair with the most one-sided distribution is *p*-xylene/benzene. Thus, even though all the guest sites are occupied by benzene when the latter is the only available guest, it is largely, but not completely, excluded when *p*-xylene, for example, is also available. This was the expectation which Jeffrey and co-workers [11] had in the preparation of several inclusion compounds of **1** by making the benzene compound and then displacing it by another guest. With *p*-xylene, at least, the displacement is not complete, so it is not surprising that these authors found evidence of incomplete occupancy by *p*-xylene in their preparation.

Attention is drawn to the pair ethylbenzene/toluene [3], not included in Table I, for which $R_S > R_L$, but for which R_L and R_S approach equality with increasing R. If the parameters given in Table II continue to be valid a little beyond the experimental range studied ($R_L > 10.5$) there is a selectivity reversal and $R_S < R_L$. Such crossover points were mentioned above, and exist in principle in all of the non-isotopic systems studied provided, of course, that Equation (1) continues to be valid beyond the range of the data.

The guest pair *p*-xylene/4-mepy deserves special mention. In the first place, 4-mepy is the only guest studied which is water soluble. Because of this, and because it was not found possible to separate quantitatively both *p*-xylene and it from the solid phases even by heating the latter under vacuum, in order to determine their relative amounts, the titrimetric procedure was devised, which was not capable of high accuracy, especially in the solid analyses.

Secondly, 4-mepy is unique in that **1** is soluble in it to the extent of about 2%, whereas it is insoluble in all the other guests except benzene. The liquid phases in this system, therefore, were also analyzed for nickel and the 4-mepy content corrected for that portion of the 4-mepy which was coordinated to the nickel. Thirdly, 4-mepy, unlike the other guests, slowly decomposes during equilibration. For these reasons the data for this system are the least accurate of all those reported, and this is evident in the scatter of the points for it in Figure 2(b): the standard deviations of m and b are ± 0.10 and ± 0.15, respectively. There is no doubt, however, that $R_{\mathrm{S}} \gg R_{\mathrm{L}}$, so that the preparation of the *p*-xylene inclusion compound of **1** in the presence of small amounts of free 4-mepy, alluded to above, is not likely to give a seriously contaminated product.

As with 4-mepy, benzene dissolves the host to a slight extent (but to a smaller degree) so the liquid phase compositions with the guest pair *p*-xylene/benzene were also corrected for host content, determined by nickel analysis.

In seeking an explanation for the order of preference shown in Table II one is tempted to think, perhaps, that its basis lies in stereoselectivity, so that the size of the guest molecule might determine the preferences observed, but this is not obvious from Table II. For example, *p*-xylene is smaller (shorter) than both *p*-bromotoluene and *p*-dichlorobenzene even though the order of selectivity is *p*-bromotoluene > *p*-xylene > *p*-dichlorobenzene. Closer examination of the equilibria involved, namely

$$\mathrm{A(in\ liquid\ solution)} \rightleftharpoons \mathrm{A(in\ solid\ solution)}$$

and

$$\mathrm{B\,(in\ liquid\ solution)} \rightleftharpoons \mathrm{B\,(in\ liquid\ solution)}$$

or, after combination,

$$\mathrm{A(in\ liquid\ solution)} + \mathrm{B\,(in\ solid\ solution)} \rightleftharpoons \mathrm{A(in\ solid\ solution)} + \mathrm{B\,(in\ solid\ solution)}$$

reveals that the position of equilibrium is determined not only by the relative fugacities of the included guests but also by those of the guests in the liquid phase, i.e., their relative vapour pressures.

If $f_{\mathrm{A}}^{\mathrm{L}}$ and $f_{\mathrm{A}}^{\mathrm{S}}$ denote the fugacities of A in the liquid and solid phases, respectively, then $f_{\mathrm{A}}^{\mathrm{L}} = f_{\mathrm{A}}^{\mathrm{S}}$ at equilibrium. Likewise $f_{\mathrm{B}}^{\mathrm{L}} = f_{\mathrm{B}}^{\mathrm{S}}$ for B. It is now assumed, as a first approximation [6], that ideal (Raoult's law) behaviour is shown for the guests in the liquid phase. This is reasonable considering their structural similarity, but may fail for the more polar guests. Then $f_{\mathrm{A}}^{\mathrm{S}} = f_{\mathrm{A}}^{\mathrm{L}} = X_{\mathrm{A}}^{\mathrm{L}} p^{\cdot}_{\mathrm{A}}$ and $f_{\mathrm{B}}^{\mathrm{S}} = X_{\mathrm{B}}^{\mathrm{L}} p^{\cdot}_{\mathrm{B}}$, where X is mole fraction and $p^{\cdot}$ is the vapour pressure of the pure liquid guest at the experimental temperature. We then write $f_{\mathrm{A}}^{\mathrm{S}} = (1/k_{\mathrm{A}})X_{\mathrm{A}}^{\mathrm{S}}$ and $f_{\mathrm{B}}^{\mathrm{S}} = (1/k_{\mathrm{B}})X_{\mathrm{B}}^{\mathrm{S}}$ where the mole fractions are on a host-free basis and k_{A}, k_{B} are a measure of the attraction of the host for the guests A and B, respectively. They have the dimensions of reciprocal pressure and are the reciprocals of a kind of activity coefficient. Although their values depend somewhat on composition we are here confining their use to those solids in which R_{S} is unity, thus making them constants for the present purpose. The implication is that k_{A}, for example, is the same in the presence of guest B as it is in the presence of any other guest, provided R_{S} is unity. It follows that

$$X_{\mathrm{A}}^{\mathrm{L}} p^{\cdot}_{\mathrm{A}} = (1/k_{\mathrm{A}})X_{\mathrm{A}}^{\mathrm{S}} \quad \text{and} \quad X_{\mathrm{B}}^{\mathrm{L}} p^{\cdot}_{\mathrm{B}} = (1/k_{\mathrm{B}})X_{\mathrm{B}}^{\mathrm{S}},$$

so

$$R_{\mathrm{S}}/R_{\mathrm{L}} = (k_{\mathrm{A}}/k_{\mathrm{B}})(p^{\cdot}_{\mathrm{A}}/p^{\cdot}_{\mathrm{B}}) \tag{2}$$

since

$$R_{\mathrm{L}} = X_{\mathrm{A}}^{\mathrm{L}}/X_{\mathrm{B}}^{\mathrm{L}} \quad \text{and} \quad R_{\mathrm{S}} = X_{\mathrm{A}}^{\mathrm{S}}/X_{\mathrm{B}}^{\mathrm{S}}.$$

Therefore

$$k_A/k_B = (R_S/R_L)(p^{\cdot}_B/p^{\cdot}_A) \tag{3}$$

to be applied where $R_S = 1$, or $X^S_A = X^S_B = 0.5$. It is evident, then, that the figures in the last column of Table II should be corrected by the factor $p^{\cdot}_B/p^{\cdot}_A$ in order to give a proper comparison of the attractions of the host for the guests. The ratio k_A/k_B is, in fact, the hypothetical selectivity (for $R_S = 1$) were the two guests to have equal vapour pressures in the pure liquid state. Except where indicated the values given in Table III, for an average room temperature of 25 °C, were calculated from the data of Stull [12]. They are used in Equation (3) to give the values of k_A/k_B shown in Table IV. By assigning an arbitrary value of 100 to

Table III. Vapour pressure of liquid guests at 25 °C

Guest(1)	$p^{\cdot}$/torr	Guest(1)	$p^{\cdot}$/torr
benzene	95.1[a]	*p*-xylene	8.77[c]
toluene	28.2	4-methylpyridine	5.0[d]
p-fluorotoluene	20.8	*p*-chlorotoluene	3.48
ethylbenzene	9.49	*p*-dichlorobenzene	1.91[e]
p-xylene-d_6	9.4[b]	*p*-bromotoluene	1.38
p-xylene-d_{10}	9.3[c]		

[a] Ref. [13]. [b] Ref. [6] recalc. [c] Ref. [10].

[d] As measured by the Ramsay and Young method and supported by data of Ref. [14] for higher temperatures.

[e] Metastable liquid.

Table IV. Guest selectivities at $R_S = 1$, corrected to equal guest vapour pressure and correlated with van der Waals length and enthalpy of inclusion

A/B	k_A/k_B	k_B ($k_A = 100$)	van der Waals length of B (nm)	Enthalpy of inclusion of 1:1 compound with B	
				from $\alpha - \mathbf{1}$(s) and B(l) (kJ/mol)	from $\beta - \mathbf{1}$(s) and B(g) (kJ/mol)
p-xylene/*p*-bromotoluene	0.153	656	1.00		
p-xylene/*p*-dichlorobenzene	0.256	390	0.98	− 34.81[a,b]	− 83.1
p-xylene/*p*-chlorotoluene	0.40	250	0.97		
p-xylene/*p*-xylene-d_6	0.94	106	0.96		
p-xylene/*p*-xylene-d_{10}	0.97	103	0.96		
p-xylene/*p*-xylene	1.00	(100)	0.96	− 34.43[b]	− 80.4
p-dichlorobenzene/*p*-chlorotoluene	1.86	–	–		
p-xylene/ethylbenzene	8.2	12.2	0.90[e]	− 32.38[c]	− 78.2
p-xylene/*p*-fluorotoluene	11.0	9.1	0.89		
ethylbenzene/toluene	14.1	–	–		
p-xylene/toluene	46.3	2.2	0.85	− 29.75[c]	− 71.3
p-xylene/4-methylpyridine	9.4	10.6	0.77	− 20.1[d]	− 68.8
p-xylene/benzene	3.0×10^4	0.0033	0.74		

[a] Calculated from measurement with solid guest, for which enthalpy of inclusion is − 16.57 kJ/mol.

[b] Ref. [2]. [c] Ref. [3]. [d] Ref. [20]. [e] Length projected on C-C-C molecular axis.

k for *p*-xylene, *k* for the other guests may be found, and Table IV also gives this quantity for the guests in the denominator of each pair listed in the first column. With one exception they are placed in the order of decreasing magnitude. Thus the guests, in the order of decreasing attraction for the host, are as follows: *p*-bromotoluene > *p*-dichlorobenzene > *p*-chlorotoluene > *p*-xylene-d_6 > *p*-xylene-d_{10} > *p*-xylene > ethylbenzene > 4-mepy > *p*-fluorotoluene > toluene > benzene, a quite different order from that obtained before applying the vapour pressure factor. It is worth noting, in the light of this, that the apparent great similarity in the selectivity behaviour of *p*-bromotoluene and *p*-chlorotoluene toward *p*-xylene, evident in the near identity of the lines in Figure 2(a), results largely from the coincidence that $k_{p\text{-chlorotoluene}}/k_{p\text{-bromotoluene}}$ nearly equals $p^{\cdot}_{p\text{-bromotoluene}}/p^{\cdot}_{p\text{-chlorotoluene}}$.

It seemed to the authors that there ought to be some parallel between the value of the *k*'s and some molecular property of the guests. Polarity, polarizability, molecular mass, and molecular size and/or shape were all considered possible properties. Polarity was immediately discarded because the polar *p*-chlorotoluene is intermediate in *k* between *p*-dichlorobenzene and *p*-xylene, both of which are non-polar. Likewise non-polar *p*-dichlorobenzene is intermediate in *k* between *p*-chlorotoluene and *p*-bromotoluene, which are polar. Polarizability, as indicated by molar refraction, was also discarded because *p*-fluorotoluene has a molar refraction (30.66 cm^3/mol) considerably less than that of *p*-xylene (35.78) and toluene (31.09) but with a *k* value intermediate between the two. (These were calculated using the following values for refractive index and density at 20 °C for *p*-fluorotoluene, *p*-xylene and toluene, respectively, taken from Beilstein: 1.4699, 1.000; 1.4958, 0.8611; 1.4961, 0.8669.) Moreover, *p*-xylene and ethylbenzene have nearly the same molar refraction (36.0) but distinctly different *k*'s. Molecular mass, expected approximately to parallel molar refraction, was also discounted for similar reasons. There remains molecular size and/or shape.

Determination of the crystal structure of the 1 : 1 inclusion compound of **1** with *p*-xylene [15] has shown that the guest molecules lie end-to-end in spiral channels, the latter intersecting at points where the carbons of the methyl groups of four adjacent *p*-xylene molecules are at the corners of a tetrahedron. Although the structures of the 1 : 1 compounds of **1** with the other guests have not been determined in such detail it will be assumed that they are the same except for the lattice constants. (The crystals are tetragonal. For the *p*-xylene compound the lattice constants are $a = 1.698$, $c = 2.362$ nm, [15] whereas for the 4-mepy compound they are $a = 1.709$, $c = 2.344$ nm [16].) Most of the guests considered here are simple mono- or *para* di-substituted benzenes. This, together with the end-to-end placement of the molecules, suggests that the length of the guest molecule may be a critical quantity in determining guest preference. For this reason the van der Waals length of the various guests has been selected as the molecular property for consideration. This quantity was estimated using available bond lengths and bond angles [17, 18] and van der Waals atomic radii [19], and are included in Table IV. They are plotted against ln *k* in Figure 3. (The choice of ln *k* was made merely to compress the wide range of values covered by *k*.) Considering the approximate nature of the theoretical approach, the somewhat arbitrary choice of $R_S = 1$ for the selectivity basis, and the uncertainties in *k*, Figure 3 strongly suggests a correlation between *k* and the van der Waals length. The only guest studied which is seriously out of line is 4-mepy. In spite of the large experimental error in this system for reasons given above, we believe the non-conformity of 4-mepy is real. It may be the result of the high polarity of this substance which may not only vitiate the assumption of ideality in the liquid phase made in the theoretical treatment, but possibly cause a different orientation of the guest molecules in the lattice while still permitting its 1 : 1 compound to be isomorphous with that of *p*-xylene.

One may speculate as to why the longer of the two molecules is preferred. With two different

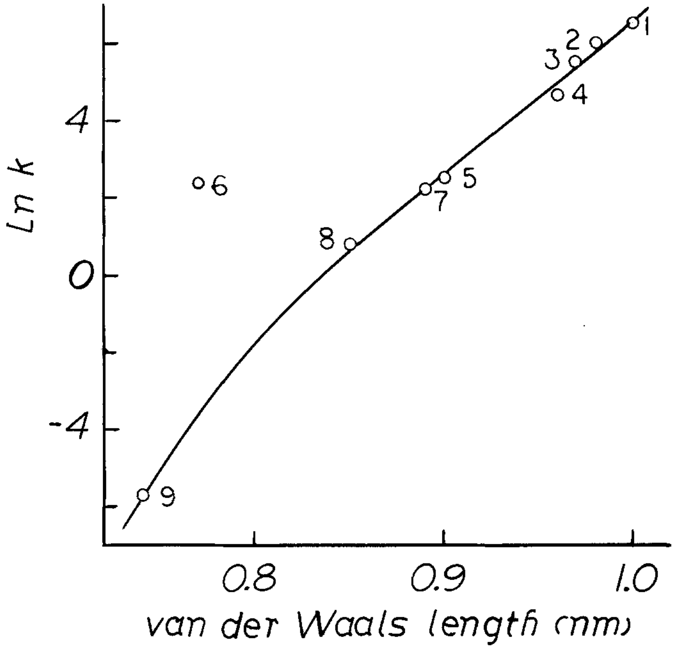

Fig. 3. Correlation between van der Waals length of guest molecule and k. 1, p-bromotoluene; 2, p-dichlorobenzene; 3, p-chlorotoluene; 4, the p-xylenes; 5, ethylbenzene; 6, 4-methylpyridine; 7, p-fluorotoluene; 8, toluene; 9, benzene.

size guest molecules occupying the same host channels it is to be expected that some unit cells will have different dimensions from the others, that a strain will be set up in the framework as a whole, and that there will be some cells containing the shorter guest which will be constrained by neighbouring larger cells to be larger than necessary for their smaller guests. This could mean that the smaller guest is held less firmly on the average than the larger guest, so that the latter has the larger k.

A comparison of Tables III and IV shows that, on the whole, the longer the guest molecule the smaller its vapour pressure. The consequence of this is that longer molecules have larger k's but smaller $p^{\cdot}$'s so that, in Equation (2), the k factor tends to compensate for the $p^{\cdot}$ factor, and R_S/R_L usually does not have very large or very small values. From the practical point of view this mitigates against one-step separations of the members of any given guest pair by inclusion.

Another correlation given in Table IV is the parallel, with the exception once again of 4-mepy, between k_B and, where available, the enthalpy of formation of the inclusion compound from the β form of **1** (the metastable, unoccupied host with the same lattice it has in the 1 : 1 compounds) and the guests in their *gaseous* state (Column 6). These were calculated from previous calorimetric measurements on the stable α form (Column 5), with the help of enthalpies of vaporization and sublimation near room temperature [20–23] and the enthalpy of conversion from α to β, 3.56 kJ/mol [24]. Because of the identical stoichiometry of all the inclusion reactions the trend shown in the enthalpy changes of Column 6 is also a trend in energy change. Furthermore, since the guest is taken here to be initially in the gaseous state where the potential energy is virtually zero, and as the guests have approximately the same shape and occupy the same channels in the host, the trend in the Column 6 values would be expected to reflect the trend in the potential energies of the included guests, and therefore the trend in k_B. They also include, however, any energy needed to dilate the β–**1** lattice – a not inconsiderable quantity [16, 25]. (An earlier attempt [3] to discover such a parallel had failed because the selectivity data had not been reduced by the vapour pressure ratios and because thermochemical data for the guests in the *liquid* form had been used.) It is worth noting that although 4-mepy is anomalous in Figure 3 and in the relationship between k_B and enthalpy of inclusion, the anomaly is not evident in that between van der Waals length and enthalpy of inclusion.

In the above discussion the various guests have been compared to each other through their relationship with *p*-xylene. If, for the triad of guests A, B, and C, $k_A/k_B = x$ and $k_A/k_C = y$ when the pairs A–B and A–C, respectively, are studied, it does not follow rigidly that k_C/k_B will be given by x/y when the pair B–C is studied. If k_C/k_B does equal x/y the implication is that the k value for a given host is the same regardless of the other guest with which it is paired. This is by no means certain because of the possibility of the mutual distortion of adjacent unit cells containing different guests in a solid solution, as discussed above. It is, however, to be expected that it will be approximately true. An opportunity to test it lies in the two pairs listed in Tables II and IV which do not include *p*-xylene. For the triad *p*-xylene(A)–*p*-dichlorobenzene(B)–*p*-chlorotoluene(C), Table IV gives $x/y = 0.26/0.40 = 0.65$, which may be compared with $1/1.86 = 0.54$ when B and C were studied together. The agreement is reasonably good. However, for the triad *p*-xylene(A)–ethylbenzene(B)–toluene(C), $x/y = 8.2/46 = 0.18$, which may be compared with $1/14.1 = 0.07$ when B and C are studied together. The agreement is poorer. This may be attributed to the ethylbenzene with its bent side chain, which gives this guest a greater effective thickness than any of the others. One may speculate that when ethylbenzene is paired experimentally with toluene the toluene-containing cells are unduly expanded. Because of this, k for toluene in the presence of *p*-xylene is bigger than it is in the presence of ethylbenzene thus requiring y to be increased in x/y and improving the agreement.

The two *p*-xylene guest pairs where the guests differ only isotopically are of interest because of the potential for the fractionation of isotopes. The k's for *p*-xylene, *p*-xylene-d_6, and *p*-xylene-d_{10}, namely 100, 106 and 103, respectively, are nearly the same within experimental error, so that the observed preference for the deuterated species in both systems was attributed [6] entirely to the vapour pressure differences. This behaviour is in marked contrast to the recent studies with the pair *p*-xylene–*p*-xylene-d_{10} [10] with the host 1,2-bis(diphenylphosphinoselenoyl)ethane (**2**), where there is a clear preference for the protiated species, and in which the k's differ by ten per cent. The difference in behaviour is attributed to the relatively loose fit of the guests in **1** but tight fit in **2**.

The practice of having 4-mepy present in the preparation of the inclusion compounds of other guests in **1** without fear of inclusion of the 4-mepy as a guest is supported by the results in Table I. Apparently its small size and consequent small k (Table IV) makes this possible, but it is clear from Table I that too large an excess should be avoided.

Finally, it is possible, by still assuming that the liquid phases all follow Raoult's law, to estimate the activity coefficients of the guests in the solid solutions of each system. The chosen standard state for each guest is that guest in the 1 : 1 inclusion compound in equilibrium with the pure liquid guest. This makes $a_A^L = a_A^S$ and $a_B^L = a_B^S$, where a is activity, if the standard states for the guests in the liquid solutions are the respective pure liquids. With $R_L = X_A^L/X_B^L$, $R_S = X_A^S/X_B^S$ the activity coefficients γ_A^S, γ_B^S, defined for A as

$$\gamma_A^S = a_A^S/X_A^S = a_A^L/X_A^S = X_A^L/X_A^S$$

and similarly for B, are then given by

$$\gamma_A^S = [R_L/(1 + R_L)][(1 + R_S)/R_S]; \; \gamma_B^S = (1 + R_S)/(1 + R_L),$$

Table V. Estimated activity coefficients for guests in solid phases at room temperature (smoothed values), (X_A^S on host-free basis)

X_A^S	γ_A^S	γ_B^S	X_A^S	γ_A^S	γ_B^S
p-dichlorobenzene(A)/*p*-chlorotoluene(B)			*p*-xylene(A)/*p*-bromotoluene(B)		
0	–	1.00	0	–	1.00
0.2	0.98	1.00	0.2	1.02	0.99
0.4	0.99	1.01	0.4	1.02	0.99
0.6	0.99	1.01	0.6	1.01	0.98
0.8	0.99	1.02	0.8	1.01	0.97
1.0	1.00	–	1.0	1.00	–
p-xylene(A)/*p*-dichlorobenzene(B)			*p*-xylene(A)/*p*-chlorotoluene(B)		
0.6	0.94	1.09	0	–	1.00
0.7	0.96	1.08	0.2	0.99	1.00
0.8	0.98	1.07	0.4	1.00	1.00
0.9	1.00	1.04	0.6	1.00	1.00
1.0	1.00	–	0.8	1.00	1.00
			1.0	1.00	–
p-xylene(A)/4-methylpyridine(B)					
0	–	1.00	*p*-xylene(A)/*p*-fluorotoluene(B)		
0.2	0.05	1.24	0	–	1.00
0.4	0.09	1.61	0.2	0.12	1.22
0.6	0.16	2.26	0.4	0.26	1.50
0.8	0.35	3.61	0.6	0.48	1.78
1.0	1.00	–	0.8	0.81	1.75
			1.0	1.00	–
p-xylene(A)/benzene(B)					
0.80	0.032	4.87			
0.85	0.085	6.19			
0.90	0.273	7.54			
0.95	0.808	4.65			
1.00	1.000	–			

and are shown in Table V for the newly reported systems at rounded mole fractions in the experimental concentration range, using the parameters for the smoothed results from Table II. The mole fractions in the solid state are on a host-free basis. For each guest pair the preferred member is, of course, the one with the smaller activity coefficient.

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References

1. W. D. Schaeffer, W. S. Dorsey, D. A. Skinner, and C. G. Christian: *J. Am. Chem. Soc.* **79**, 5870 (1957).
2. M. I. Hart, Jr. and N. O. Smith: *J. Am. Chem. Soc.* **84**, 1816 (1962).
3. Sr. M. J. Minton and N. O. Smith: *J. Phys. Chem.* **71**, 3618 (1967).
4. S. E. Ofodile, R. M. Kellett, and N. O. Smith: *J. Am. Chem. Soc.* **101**, 7725 (1979).
5. S. E. Ofodile and N. O. Smith: *Anal. Chem.* **53**, 904 (1981).

6. S. E. Ofodile and N. O. Smith: *J. Phys. Chem.* **87**, 473 (1983).
7. A. E. Hill, G. S. Durham, and J. E. Ricci: *J. Am. Chem. Soc.* **62**, 2723 (1940).
8. H. W. Bakhius Roozeboom: *Z. Physik. Chem.* **8**, 521 (1891).
9. A. V. Logan and D. W. Carle: *J. Am. Chem. Soc.* **74**, 5224 (1952).
10. S. Saba and N. O. Smith: *J. Phys. Chem.* **89**, 5414 (1985).
11. D. Belitskus, G. A. Jeffrey, R. K. McMullan, and N. C. Stephenson: *Inorg. Chem.* **2**, 873 (1963).
12. D. R. Stull: *Ind. Eng. Chem.* **39**, 517 (1947).
13. G. Jakli, P. Tzias, and W. A. Van Hook: *J. Chem. Phys.* **68**, 3177 (1978).
14. E. F. G. Herington and J. F. Martin: *Trans. Faraday Soc.* **49**, 154 (1953).
15. J. Lipkowski, K. Suwinska, G. D. Andreetti, and K. Stadnicka: *J. Mol. Struct.* **75**, 101 (1981).
16. J. Lipkowski and S. Majchrzak: *Rocz. Chem.* **49**, 1655 (1975).
17. *Tables of Interatomic Distances and Configuration in Molecules and Ions.* Special Publication No. 11. The Chemical Society, London (1958).
18. *Tables of Interatomic Distances and Configuration in Molecules and Ions.* Supplement 1956–1959. Special Publication No. 18. The Chemical Society, London (1965).
19. L. Pauling: *The Chemical Bond*, Cornell University Press, Ithaca, N.Y. (1967).
20. J. Chajn, J. Lipkowski, and W. Zielenkiewicz: *Rocz. Chem.* **51**, 1431 (1977).
21. P. N. Walsh and N. O. Smith: *J. Chem. Eng. Data* **6**, 33 (1961).
22. *International Critical Tables*, v. 5, pp. 133, 137, McGraw-Hill Book Co., New York, N.Y. (1929).
23. J. H. Hildebrand, J. M. Prausnitz, and R. L. Scott: *Regular and Related Solutions*, p. 214, Van Nostrand Reinhold Co., New York, N.Y. (1970).
24. J. Lipkowski and J. Chajn: *Rocz. Chem.* **51**, 1443 (1977).
25. P. Starzewski, W. Zielenkiewicz, and J. Lipkowski: *J. Incl. Phenom.* **1**, 223 (1984).