SELECTIVITY OF THE HOST Ni(4-mepy)$_4$(NCS)$_2$ TOWARDS AROMATIC GUESTS

H. L. Wiener, L. Ilardi, P. Liberati, L. Dengler,
S. A. Jeffas, S. Saba, and N. O. Smith
Department of Chemistry
Fordham University
Bronx, New York 10458-5198
U. S. A.

The host Ni(4-mepy)$_4$(NCS)$_2$, $\underline{I}$, forms isomorphous 1:1 inclusion compounds with many monocyclic aromatic guests. In continuing attempts to determine the basis for the selectivity shown by $\underline{I}$ towards pairs of such guests, distribution data between solid and liquid phases were reported for seven ternary systems at room temperature. These consist of $\underline{I}$, p-xylene, and each of the following in turn: p-bromotoluene, p-chlorotoluene, p-fluorotoluene, p-dichlorobenzene, 4-methylpyridine and benzene, as well as the system $\underline{I}$—p-chlorotoluene—p-dichlorobenzene. The results, as well as those already published, were reviewed.

The distribution data were given in the form of $\underline{R}_L$ and $\underline{R}_S$, where $\underline{R}_L$ is the mole ratio of the guests in the liquid and $\underline{R}_S$ that in the coexisting solid phase. Since ln $\underline{R}_L$ appears to be a linear function of ln $\underline{R}_S$ the data were fitted to

$$\ln \underline{R}_S = \underline{m} \ln \underline{R}_L + \underline{b}$$

giving the values of the parameters $\underline{m}$ and $\underline{b}$ shown in Table I. As $\underline{R}_S/\underline{R}_L$ is not, in general, a constant for any one system, its value when $\underline{R}_S$ = 1 was chosen, somewhat arbitrarily, as a measure of the selectivity in each system. This quantity is also included in Table I and listed in the order of increasing value. For those guest pairs in which p-xylene is one member, the order given in the table is therefore the apparent order of preference of the other guests in the hierarchy of selectivity; namely, p-xylene-d$_6$ > p-xylene-d$_{10}$ > p-bromotoluene > p-chlorotoluene > p-dichlorobenzene........ > benzene. However, this order bears no obvious relation to any molecular property of these guests.

Table I. Parameters for $\ln \underline{R}_S = \underline{m} \ln \underline{R}_L + \underline{b}$.

Guest pair	$\underline{m}$	$\underline{b}$	$\underline{R}_S/\underline{R}_L$ ($\underline{R}_S = 1$)
p-xylene/p-xylene-d$_6$	0.97	-0.12	0.88
p-xylene/p-xylene-d$_{10}$	.97	- .09	.91
p-xylene/p-bromotoluene	1.00	- .03	.97
(p-xylene/p-xylene	1.00	0	1.00)
p-xylene/p-chlorotoluene	0.999	.007	1.01
p-dichlorobenzene/			
p-chlorotoluene	1.00	.02	1.02
p-xylene/p-dichlorobenzene	.95	.15	1.18
p-xylene/p-fluorotoluene	.64	.99	4.63
ethylbenzene/toluene	.60	.94	4.75
p-xylene/ethylbenzene	1.16	2.3	7.56
p-xylene/toluene	.64	1.72	14.4
p-xylene/4-methylpyridine	.75	2.1	16.5
p-xylene/benzene	.32	2.56	2790

In order to reveal such a relation a quasi-thermodynamic approach was presented, based on the equilibria:

Guest A in liquid $\rightleftharpoons$ Guest A in solid
Guest B in liquid $\rightleftharpoons$ Guest B in solid
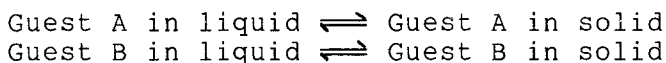
If $\underline{f}$ is fugacity then $\underline{f}_A^L = \underline{f}_A^S$ and $\underline{f}_B^L = \underline{f}_B^S$, where L and S refer to coexisting liquid and solid phases, respectively. For $R_S = 1$, and assuming that Raoult's law applies to the guests in the liquid phase, $\underline{f}_A^L = \underline{p}_A^\cdot \underline{x}_A^L$ and $\underline{f}_B^L = \underline{p}_B^\cdot \underline{x}_B^L$, where $\underline{p}_A^\cdot$ and $\underline{p}_B^\cdot$ are the vapour pressures of the pure liquid A and B.   Furthermore, writing $\underline{f}_A^S = (1/\underline{k}_A)\underline{x}_A^S$ and $\underline{f}_B^S = (1/\underline{k}_B)\underline{x}_B^S$ when $R_S = 1$, gives

$$\underline{k}_A/\underline{k}_B = (\underline{R}_S/\underline{R}_L)(\underline{p}_B^\cdot/\underline{p}_A^\cdot)$$

in which $\underline{k}_A$ and $\underline{k}_B$ are measures of the attraction of the host for the respective guests. Thus, multiplying the $\underline{R}_S/\underline{R}_L$ values in Table I by $\underline{p}_B^\cdot/\underline{p}_A^\cdot$ yields $\underline{k}_A/\underline{k}_B$, a quantity which compares the host-guest attractions for A and B. Values of $\underline{k}_A/\underline{k}_B$ are shown in Table II, in which, with two obvious exceptions, A represents p-xylene and B the guest paired with it. Assigning an arbitrary value of 100 to $\underline{k}$ for p-xylene yields the values of $\underline{k}_B$, also given in the table.

The $\underline{k}$'s, with the exception of that for 4-methylpyridine, vary smoothly with the estimated van der Waals length of the guest molecule. Thus it is the latter property which

appears to determine primarily the selectivity, the longer
of the two competing guest molecules being preferred over
the shorter —— after correcting for the differences in
their vapour pressures. An explanation for this is
attempted.

Table II. Correlation between corrected guest
selectivities and van der Waals length of guest molecule

A/B	$\underline{k}_A/\underline{k}_B$	$\underline{k}_B$	length of B (nm)
p-xylene/p-bromotoluene	0.153	656	1.00
p-xylene/p-dichlorobenzene	.256	390	0.98
p-xylene/p-chlorotoluene	.40	250	.97
p-xylene/p-xylene-$\underline{d}_6$	.94	106	.96
p-xylene/p-xylene-$\underline{d}_{10}$	.97	103	.96
p-xylene/p-xylene	1.00	(100)	.96
p-dichlorobenzene/p-chlorotoluene	1.86	–	–
p-xylene/ethylbenzene	8.2	12.2	.90
p-xylene/p-fluorotoluene	11.0	9.1	.89
ethylbenzene/toluene	14.1	–	–
p-xylene/toluene	46.3	2.2	.85
p-xylene/4-methylpyridine	9.4	10.6	.77
p-xylene/benzene	3.0×10^4	0.0033	.74

        The behaviour noted with $\underline{I}$, where the fit of the guests
in the host lattice is loose was contrasted with that ob-
served with other hosts where the fit is tight.
        The assumption of ideality in the liquid phase permits
the calculation of the activity coefficients of the guests
in the solid phases. These were also presented. For each
guest pair the preferred member is the one with the smaller
activity coefficient.