AD-A127 599 MOLECULAR ASSOCIATION AND MONOLAYER FORMATION OF SOLUBLE PHTHALOCYANINE COMPOUNDS(U) NAVAL RESEARCH LAB WASHINGTON DC A W SNOW ET AL. 20 APR 83 1/1

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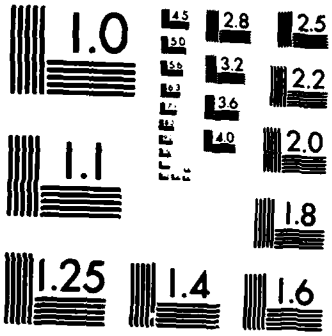
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Molecular Association and Monolayer Formation of Soluble Phthalocyanine Compounds

by

Arthur W. Snow
N. Lynn Jarvis

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Arthur W. Snow
N. Lynn Jarvis

Chemistry Division
Naval Research Laboratory
Washington, D.C. 20375

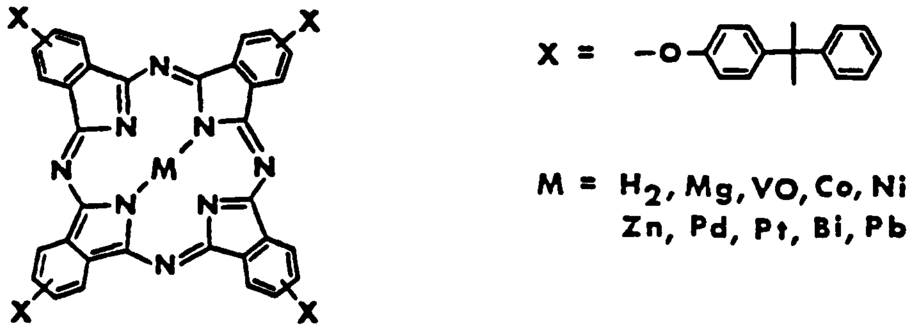
ABSTRACT

A series of H_2, Mg, VO, Co, Ni, Cu, Zn, Pd, Pt, Bi and Pb 4, 4', 4'', 4'''-tetracumylphenoxy phthalocyanine compounds, $MPcX_4$, was synthesized. By vapor pressure osometry measurements of toluene solutions at 65°C, all $MPcX_4$ compounds were dimeric complexes except $PbPcX_4$ which is monomeric and Cu,Ni,Pd and $PtPcX_4$ which form larger complexes ranging from 2.7 to 4.1 molecular units. Each $MPcX_4$ forms a stable Langmuir–Blodgett monolayer to film pressures of 20 mN/m and force-area curves indicate a dense packing of phthalocyanine units with molecular areas increasing with complex size.

Molecular Association and Monolayer Formation of Soluble Phthalocyanine Compounds

Arthur W. Snow
N. Lynn Jarvis
Chemistry Division
Naval Research Laboratory
Washington, D.C. 20375

Recent advances in understanding the chemistry and physics of phthalocyanine compounds include reports of vapor induced electrical conductivity[1], electronic switching between conducting states[2], photovoltaic effects[3], oxidative and photoxidative catalytic activity[4] and electrochromism[5]. These phenomena involve surface interactions with chemical vapors, electromagnetic irradiation and electrical contacts. To study these interactions an ideal physical form would be phthalocyanine monolayers of known concentration and orientation deposited on interdigital microelectrodes[6]. The mono and multimolecular layer (Langmuir-Blodgett) approach to studying organic films is of considerable current interest[7]. Such studies require soluble phthalocyanine compounds and a knowledge of their solution and solid-state ordering. We wish to report the synthesis of eleven members of a new family of tetracumylphenoxy substituted phthalocyanines, their degrees of association in solution and their monolayer forming properties at the water/air interface.



Our new findings include the direct observation of a dimeric complex as the predominant degree of association for most of the phthalocyanine compounds in solution, a d^8 effect that promotes degrees of association greater than two for the Ni, Pd and Pt phthalocyanines, a large ion effect that prevents dimer formation of the Pb phthalocyanine and the formation of stable monomolecular phthalocyanine films whose packing densities at the interface relate to the degree of association.

The tetracumylphenoxy phthalocyanine compounds, $MPcX_4$, were synthesized in evacuated sealed tubes at 280°C by reacting cumylphenoxyphthalonitrile[8] with a four fold molar excess of hydroquinone for H_2PcX_4 [9a], $PdCl_2$ for $PdPcX_2$, $PtCl_2$ for $PtPcX_4$, PbO for $PbPcX_4$[9b] and the appropriate acid etched metal turnings or powder for the remaining $MPcX_4$ compounds. The cumylphenoxy group dominates the solubility properties of these compounds. They are all soluble in aromatic, chloroalkane and cyclic ether solvents and were purfied by column chromatography on neutral alumina. Elemental analysis (C, H, N, M) and spectroscopic data (electronic, infrared, ^1H NMR [10], ESR) are consistent with the assigned structures.

The number average degree of association in toluene was measured by vapor pressure osmometry[11] as the apparent molecular weight divided by the molecular weight calculated from the assigned structure (Figure 1). The linearity of the plot indicates the degree of association does not significantly vary over the concentration range 3×10^{-3} to 2×10^{-2} M, and the slope is related to the solvent-solute interaction. Most of the $MPcX_4$ compounds are dimeric complexes in solution. The exceptions are $PbPcX_4$ which is unimolecular and the Cu, Ni, Pd and Pt phthalocyanines which form progressively higher order complexes.

That phthalocyanine compounds are dimeric complexes in organic solvents was postulated by Bernauer and Fallab[12] and further advanced by Monahan et al[13] on the basis of electronic and ESR spectroscopies and solvent polarity effects. Their systems were limited to copper, vanadyl and zinc metals, and they did not consider the possibility of higher order complexes. We confirm by direct solution activity measurements that dimeric association is a general trend of phthalocyanine compounds in solution and add that specific metal ion effects can superimpose on this dimerization tendency. These metal ion effects operate when the complexed metal ion has sufficient size or proper electronic structure to transcend the π orbitals of the phthalocyanine ring and interact with other molecular units. Table I presents the number average degree of association, metal ion radius and d electronic configuration of the $MPcX_4$ compounds investigated. To exert a strong influence on association from a consideration of size only, the metal ion electronic radius must perturb the phthalocyanine electronic structure or extend beyond the distance of maximum π electron density[14,15] of the phthalocyanine ring. Of the $MPcX_4$ compounds studied, $PbPcX_4$ has by far the largest ionic radius. Spectroscopic and crystallographic data on PbPc indicate that the lead ion is displaced 0.4 Å from the plane of the phthalocyanine ring[2a,16,17]. This structural distortion of symmetry may disrupt the general tendency of the phthalocyanine ring to form dimers. Further, the $5d^{10}6s^2$ electronic configuration of the plumbus ion would not be expected to promote coordination with another PbPcX unit. On the other hand, the $MPcX_4$ compounds with the d^8 configuration have an enhanced capacity to form complexes of a higher order than two molecular units, and this effect increases with metal ion size. It is well known that square planar complexes of d^8 Ni(II), Pd(II) and Pt(II) can form stacked columns with some partial metal-metal bonding through an axial interaction in the solid state[18]. Krogmann[19] has applied the valence bond approach to describe the stacking of d^8 square planar platinum complexes and proposed an axial bonding through the hybridized d_{z^2} and p_z orbitals in an excited high spin electronic state. His scheme would predict paramagnetism for analogously bonded d^8 phthalocyanine complexes in solution, and, indeed, preliminary ESR measurements show very strong signals (10^{19} spin/gram) which decrease progressively from the Ni to the Pd and Pt complexes. This would be consistent with a bond pairing of axial d electrons of the internal phthalocyanine units of larger stacked complexes. Regarding the phthalocyanines in general, NiPc is somewhat unique in that exceptionally strong ESR signals at g = 2 have been observed in both solution[20,21] and the solid-state[21,22].

Concentration and solvent dependent variations in electronic spectra have been interpreted as due to the formation of dimeric phthalocyanine complexes in the cases of $CuPcX'_4$, $VOPcX'_4$ and $ZnPcX'_4$($X' = SO_2NH(CH_2)_{17}CH_3$) in organic solvents[13] and of $CuPcX''_4$ and $CoPcX''_4$ ($X'' = SO_3^-$) in aqueous and mixed aqueous-organic solvents[12,23]. The spectroscopic observation is a narrow monomer absorption band between 650 and 700 nm superimposed on a broad dimer absorption with a partially resolved maximum at a slightly shorter wavelength. The higher order Ni, Pd and Pt complexes of our $MPcX_4$ system display a progressive enhancement of this broad shorter wavelength absorption when compared with a ''well-behaved'' dimer such as $ZnPcX_4$ or monomer such as $PbPcX_4$ (Figure 2). Only the $PbPcX_4$ electronic spectrum follows Beer's law, which would be expected as it exhibits no complex equilibria. The interpretation of the $CuPuX'_4$ electronic and ESR spectra as a dimer[13b,24] has been disputed in favor of a higher complex on the basis of a more comprehensive ESR study[20]. Our results support the latter position.

Monomolecular films of the metal substituted cumylphenoxy phthalocyanines, where M = H_2, Co,Cu,Ni,Pd and Pt, were spread at the water/air interface from benzene solution[25]. Surface tension was monitored by the Wilhelmy plate technique to + 0.05 mN/m. The force-area curves are presented in Figure 3. Each of the phthalocyanine compounds was discovered to form stable, reproducible films to film pressures of 20 mN/m or higher.

Two outstanding features of the monolayer data of Figure 3 are first, that the complexing metals have a pronounced effect on the area occupied per phthalocyanine molecule, and second, that all the phthalocyanine derivatives occupy areas that are remarkably small. The areas/molecule are consistent with cofacial orientation, with the planar rings oriented at a significant angle out of the water/air interface. Cofacial orientation is consistent with the electronic spectra of the compounds in solution and could readily give rise to strong metal-metal interactions between adjacent molecules. The effect of the metal atoms on phthalocyanine packing in the monolayer relates at least qualitatively to the degree of association given in Figure 1. The metals giving the highest degree of association, Ni, Pd and Pt, also give the largest area/molecule at equivalent film pressures, and in the same order. The correlation indicates that the electronic interactions giving rise to the different degrees of association in solution are also operative in the monolayer regime. Those derivatives giving dimer formation in solution (H_2 and Co), and the somewhat more associated Cu compound, gave evidence of closer packing at the water/air interface; however, with significant individual differences.

If the phthalocyanine solution complexes are considered to have a columnar structure of cofacially stacked rings and to exist as such in the monolayer, then it is resonable to presume that the smaller, shorter aggregates would pack more efficiently than the larger, longer ones. Such a model would be consistent with the molecular area ordering of the Pt, Pd and Ni complexes. The variations in molecular area of the dimeric complexes may be due to additional ordering brought about in transition from the solution to the solid-state monolayer. Notably, polymorphs attributable to dimer structures, which are distinct from the commonly encountered α and β phthalocyanine crystalline forms, have been proposed for CuPc[24] and H_2Pc[26]. Currently we are developing characterization techniques for these monolayers.

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Table I

Number Average Degree of Association (DA), Ionic Radius (R), and d Electronic Configuration of $MPcX_4$ Compounds

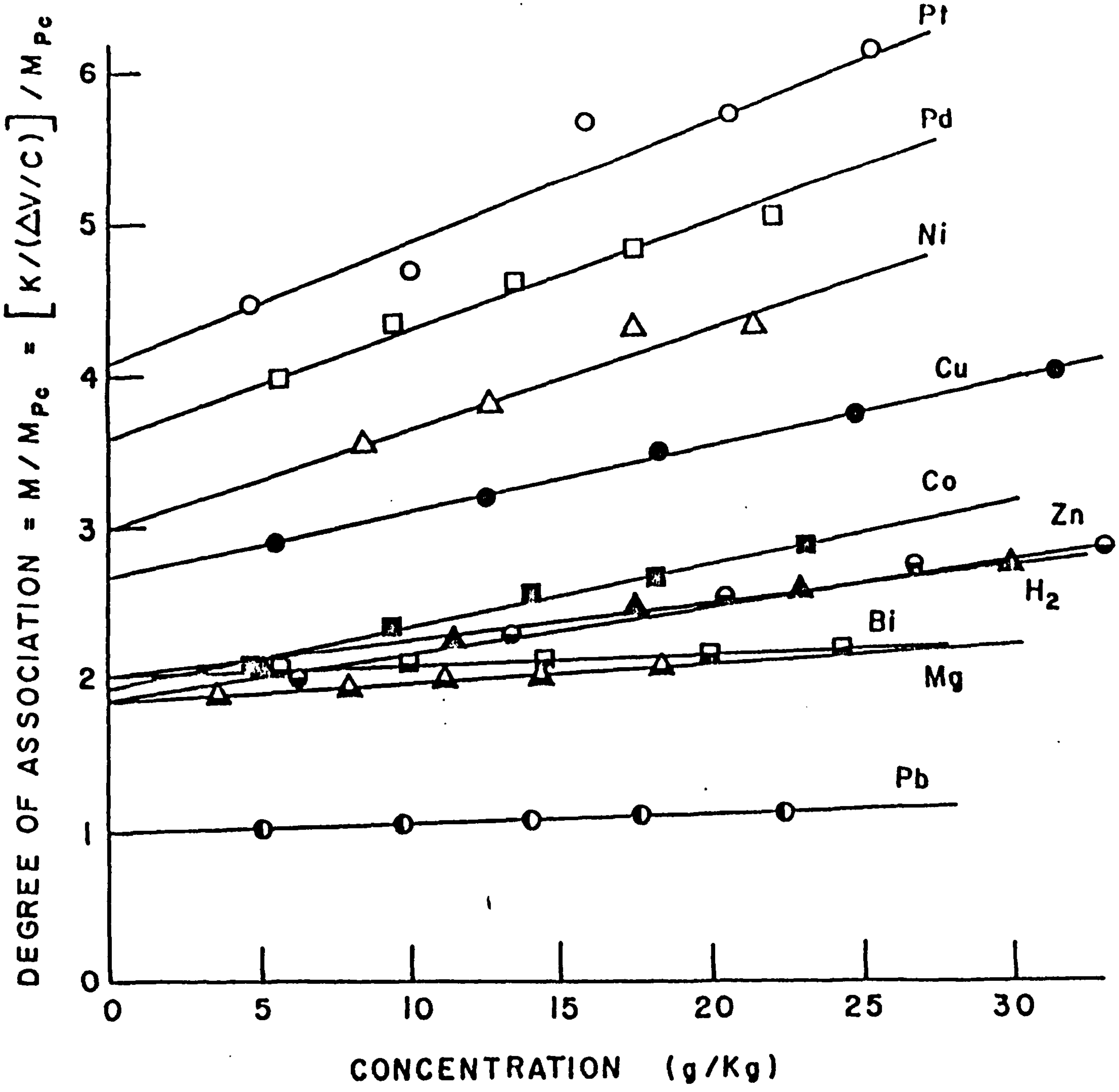
M	DA	R(A)	d
H_2	2.0	-	-
Mg^{2+}	1.9	.66	-
VO^{2+}	1.9	.88	d^1
Co^{2+}	2.0	.72	d^7
Ni^{2+}	3.0	.69	d^8
Pd^{2+}	3.6	.80	d^8
Pt^{2+}	4.1	.80	d^8
Cu^{2+}	2.7	.72	d^9
Zn^{2+}	1.9	.74	d^{10}
Bi^{3+}	2.0	.96	d^{10}
Pb^{2+}	1.0	1.20	d^{10}

LEGENDS FOR FIGURES

Figure 1. Number average degree of association (vapor pressure osmometry molecular weight divided by monomeric molecular weight) of $MPcX_4$, compounds in toluene solution at 65°C.

Figure 2. Electronic spectra of monomeric $PbPcX_4$, dimeric $ZnPcX_4$ and progressively higher order (Ni, Pd, Pt) $MPcX_4$ complexes.

Figure 3. Langmuir-Blodgett force-area curves of $MPcX_4$ compounds.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Pd
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Cu
Co
Zn
H_2
Bi
Mg
Pb
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2
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15
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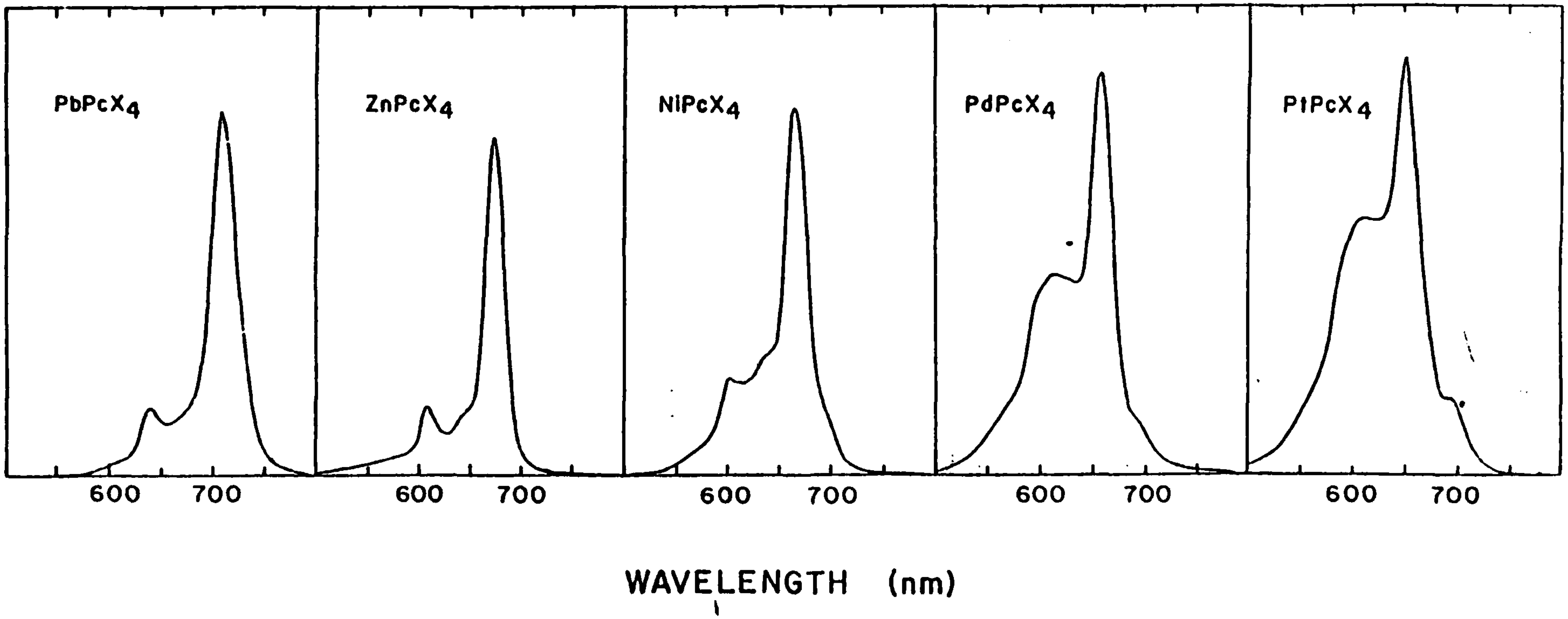
DEGREE OF ASSOCIATION = M/M_{Pc} = $[K/(\Delta V/C)]/M_{Pc}$
CONCENTRATION (g/Kg)



PbPcX4
ZnPcX4
NiPcX4
PdPcX4
PtPcX4
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700
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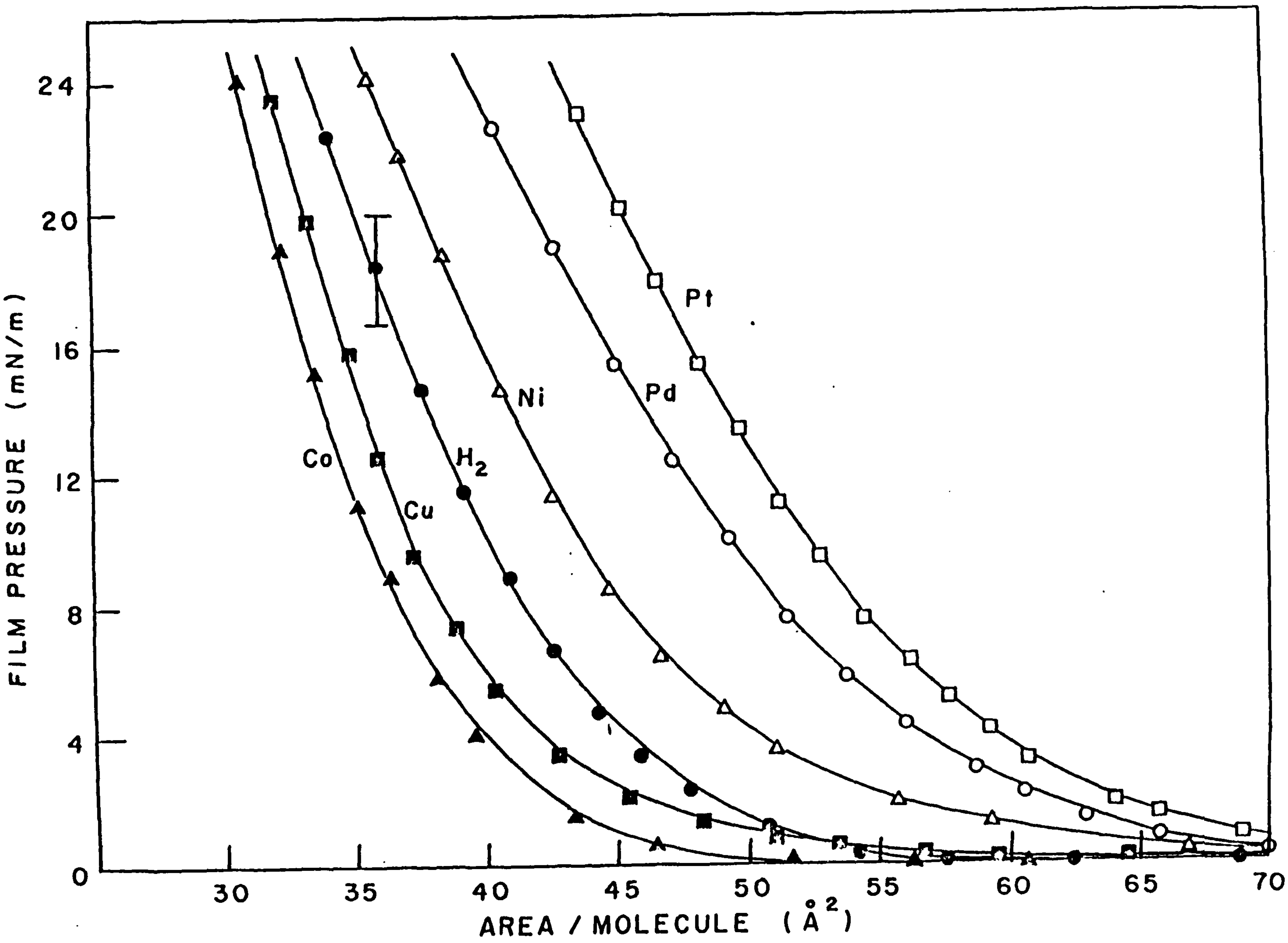
WAVELENGTH (nm)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