

# JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

## Spectral Shifts in Acid–Base Chemistry. 1. Van der Waals Contributions to Acceptor Numbers<sup>1,2</sup>

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**Abstract:** The <sup>31</sup>P NMR spectra of triethylphosphine oxide (Et<sub>3</sub>PO) undergoes a shift upon interaction in solution with adjacent molecules. The oxygen of Et<sub>3</sub>PO is a strong electron donor and readily forms acid–base complexes with electron acceptors, with a consequent downfield shift in the <sup>31</sup>P NMR spectrum ( $\Delta\delta^{ab}$ ). We find that the <sup>31</sup>P NMR spectrum also is shifted downfield appreciably by van der Waals (largely dispersion force) interactions with solvents ( $\Delta\delta^d$ ). These two contributions are also observed in the heats of mixing of binary solutions (where  $\Delta H_M = \Delta H_M^d + \Delta H_M^{ab}$ ), in the frequency shifts of infrared spectra (where  $\Delta\nu = \Delta\nu^d + \Delta\nu^{ab}$ ), and in the contributions to the surface tension of liquids (where  $\gamma = \gamma^d + \gamma^{ab}$ ). Mayer and Gutmann used the total <sup>31</sup>P NMR spectral shift of Et<sub>3</sub>PO upon interaction with test liquids for the assignment of acceptor numbers (AN). However, even basic liquids such as pyridine have large AN values because of the strong van der Waals attractive forces of liquid pyridine. This paper offers a method of correcting AN values for the van der Waals contribution to the chemical shift on the basis of the determination of the  $\gamma^d$  values from measurements of the surface and interfacial tensions of the test liquids. Values of  $\Delta\delta^{ab}$ , AN–AN<sup>d</sup>, and AN\* (the heat of acid–base interaction of Et<sub>3</sub>PO with acidic liquids, in kcal/mol) were determined for 30 liquids, for which  $\Delta\delta^{ab} = \delta_0 + 7.37 - 0.312\gamma^d$ .

Intermolecular interactions in liquids always involve some degree of van der Waals attractive forces, especially from nearest- and next-nearest-neighbor molecules. The classical van der Waals attractive forces occur between pairs of molecules having near collisions in gases where the approaching molecular pairs can orient dipoles to maximize attractive forces. The attractive force between an interacting pair of gas molecules can result from three kinds of interactions: (1) the ever-present London dispersion forces (proportional to the square of the molecular polarizability), (2) the Keesom dipole–dipole interactions if dipoles are present, and (3) the Debye interactions of dipoles with the dipoles induced in adjacent molecules. The attractive energy of each of these three terms is proportional to the inverse sixth power of the intermolecular distance of the colliding pair of gas molecules.

In liquids every molecule has many nearest- and next-nearest-neighboring molecules, usually much closer than the distance

of closest approach in gases. Perhaps because of the large number of nearest-neighbor molecules in liquids, the dipole–dipole interactions in liquids provide a much smaller contribution to the van der Waals interactions than in gases, as is evidenced by a comparison of the dipole–dipole interactions in water vapor versus liquid water. London calculated that in water vapor where the dipoles in pairs of approaching molecules are mutually oriented to maximize attractive interactions, 76% of the van der Waals intermolecular interaction energy results from dipole interactions.<sup>3</sup> None of this energy results from hydrogen bonding, for hydrogen bonds occur only at the very close intermolecular distances observed in ice or liquid water. However, in liquid water about 70% of the intermolecular attractive energy results from hydrogen bonds (as estimated from the surface free energy  $\gamma$  or from the cohesive energy density, CED),<sup>4</sup> about 28% results from the dispersion-force contribution to van der Waals interactions, and only 2.4% results from dipole contributions to van der Waals interactions (as calculated from the static dielectric constant of water by the

(1) Presented at the 195th National Meeting of the American Chemical Society, Toronto, ON, June, 1988; *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1988**, 29, (1), 188–189.

(2) This paper is dedicated to the late Prof. John A. Manson, whose enthusiastic support of acid–base research projects is deeply appreciated.

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Lifshitz approach).<sup>5,6</sup> Thus, the proportion of intermolecular forces due to dipole interactions falls from 76% for water vapor to 2.4% for liquid water at room temperature.

The magnitude of the van der Waals contribution to the surface tension of water ( $\gamma^d$ ) has been determined from measurements of the work of adhesion  $W_{12}$  between water (1) and saturated hydrocarbons (2):

$$W_{12} = \gamma_1 + \gamma_2 - \gamma_{12} = 2(\gamma_2^d \gamma_1^d)^{1/2} \quad (1)$$

This equation was initially tested most successfully for the calculation of the interfacial tension between water and mercury<sup>4</sup> and is widely accepted.<sup>7</sup> For 25 years the term  $\gamma^d$  determined from eq 1 has been described as the London dispersion force contribution to the surface tension, and  $\gamma^d$  was shown to be proportional to the Hamaker constant for prediction of interfacial van der Waals attractive forces.<sup>4</sup> However, advances in the study of interfacial forces have shown that, with liquids of high static dielectric constant, the van der Waals interactions (and therefore  $\gamma^d$ ) have a nondispersive contribution; at room temperature this contribution to the van der Waals interactions amounts to 8% for water, 6% for acetone, and 0.9% for polystyrene.<sup>5</sup> Because of this discrepancy Chaudhury and co-workers have proposed to change the symbol  $\gamma^d$  to  $\gamma^{LW}$  where the superscript "LW" refers to the London-van der Waals interactions.<sup>6</sup> In this paper we shall continue the use of  $\gamma^d$  but refer to it as the van der Waals contribution to the surface free energy of a liquid or solid.

The hydrogen-bonding contribution to the surface free energy of water ( $\gamma^{ab}$ ) is symbolized with an "ab" superscript because hydrogen bonds have been shown to be a typical "hard" subset of the Lewis hard and soft acid-base (HSAB) interactions. Hard acid-base interactions are dominated by electrostatic interactions, and hydrogen bonds have been shown to be predominantly electrostatic attractions between negatively charged hydrogen acceptors (electron donors) and positively charged (active) hydrogens.<sup>8,9</sup> This view does not mean that hydrogen bonds are dipole-dipole attractions, for Pimental and McClellan's 1960 book *The Hydrogen Bond*<sup>10</sup> showed that the energy of hydrogen bonds is entirely independent of dipole moments and depends only on the acidity of the hydrogen donor and the basicity of the hydrogen acceptor.

In studies of the heats of mixing of a solvent and solute ( $\Delta H_M$ ), the observed heats always have endothermic van der Waals contributions ( $\Delta H_M^d$ ) and sometimes have acid-base contributions ( $\Delta H_M^{ab}$ ), which are exothermic when acid-base complexes are formed, and endothermic when such complexes are dissociated:

$$\Delta H_M = \Delta H_M^d + \Delta H_M^{ab} \quad (2)$$

In the study of intermolecular interactions between two components such as an acid and a base, it is important to recognize whether or not the acid-base interaction takes place in a solvent or not. If an acid and a base interact with each other in dilute solution in a neutral solvent, the van der Waals contribution to intermolecular interactions remains constant, as Drago pointed out many years ago.<sup>11</sup> However, this paper is devoted to two-component systems such as those used by Mayer and Gutmann for the estimation of acceptor numbers, where the interactions of acidic liquids with  $\text{Et}_3\text{PO}$  were determined from NMR spectral shifts measured with the  $\text{Et}_3\text{PO}$  dissolved directly in the acidic liquid and without any solvent to control the van der Waals contributions to interaction energies.<sup>12</sup>

The endothermic heats of mixing of liquids having only van der Waals interactions ( $\Delta H_M^d$ ) have been characterized extensively by Hildebrand's solubility parameters (the square root of the cohesive energy density, CED, the energy of vaporization per unit volume) for prediction of heats of mixing of two-component systems.<sup>13</sup> As Hildebrand clearly pointed out, the solubility parameter predictions hold for systems having only van der Waals interactions, and they cannot be used for systems with specific interactions such as hydrogen bonding.

On the other hand, the most extensive study of the exothermic interactions of acids and bases (By Drago and others)<sup>14-19</sup> was done in neutral solvents where the van der Waals contributions canceled out. In this paper we discuss the Mayer/Gutmann studies of acid-base interaction, all done in two-component systems where the van der Waals contribution is very significant.

The relation of spectral shifts to heats of mixing was pointed out in the late 1930s by Badger and Bauer,<sup>20</sup> on the basis of a study of the infrared frequency shift for the -OH stretching frequency. Drago and others expanded this concept and used it to predict interaction energies successfully. The -OH and -NH infrared spectral shifts of hydrogen acids were correlated with calorimetric heats of mixing of dilute solutions of acid with an excess of base in neutral ("poorly solvating") solvents such as cyclohexane or carbon tetrachloride. In Drago's studies the heats of acid-base interaction were correlated with his  $E$  and  $C$  equation:

$$-\Delta H^{ab} = E_A E_B + C_A C_B \quad (3)$$

The infrared shift of the carbonyl group of ethyl acetate upon complexation with test acids in a neutral solvent was known to be directly proportional to the heats of acid-base complexation of the basic carbonyl oxygen with the test acid,<sup>21,22</sup> but in simple solutions of ethyl acetate in various solvents (two-component systems), Fowkes and co-workers found that the carbonyl infrared shift also has an appreciable van der Waals shift, proportional to the van der Waals contribution to the surface tension ( $\gamma^d$ ) or to the cohesive energy density ( $\delta^2$ ) of the solvents.<sup>23</sup> Therefore in two-component systems

$$\Delta \nu_{\text{CO}} = \Delta \nu_{\text{CO}}^d + \Delta \nu_{\text{CO}}^{ab} \quad (4)$$

The van der Waals infrared shifts are always observed in  $-\text{C}=\text{O}$ ,  $-\text{P}=\text{O}$ ,  $-\text{S}=\text{O}$ , and  $-\text{N}=\text{O}$  stretching frequencies, but are less obvious in the -OH or -NH stretching frequencies, perhaps because the polarizability of the  $=\text{O}$  oxygen in these groups is so much greater than that of the hydrogen, and the dispersion force interactions are a function of the square of the polarizability of the interacting atoms.

Mayer and Gutmann<sup>12,24-27</sup> introduced the concept of using the  $^{31}\text{P}$  NMR chemical shift of triethylphosphine oxide ( $\text{Et}_3\text{PO}$ ), a Lewis base, for characterizing the electrophilic (or acidic) nature of solvents. It was proposed that an empirical parameter, the acceptor number (AN), be used to indicate the relative Lewis

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**Table I.** Van der Waals Contribution to IR  $\nu_{\text{P=O}}$  and NMR  $^{31}\text{P}$  Shift

$\text{Et}_3\text{PO}^-$ in	$\gamma^d$ (mJ/m <sup>2</sup> )	$\nu_{\text{P=O}}$ (cm <sup>-1</sup> )	$^{31}\text{P}$ $\delta$
vapor	0.0	1209	
hexane	18.4	1191	-1.68
benzene	28.9	1180	1.81
$\text{CCl}_4$	27.0	1177	1.96
pyridine	38.0	1170	4.36
$\text{CH}_2\text{I}_2$	50.8	1155	8.52

acidity of solvents. The acceptor number was based on the measured  $^{31}\text{P}$  chemical shift of  $\text{Et}_3\text{PO}$  dissolved in the solvent being evaluated (a two-component system). The acid-base interaction of  $\text{Et}_3\text{PO}$  with an electrophilic site occurs by electron donation at the oxygen atom of the  $\text{P=O}$  group. This causes a decrease in the electron density at the phosphorus atom and a corresponding downfield  $^{31}\text{P}$  NMR shift. On the basis of the magnitude of this shift, the acceptor number was calculated and assigned to the solvent, and it was assumed that the acceptor number was a measure of the acidity or electrophilicity of the solvent.

NMR shifts, like IR shifts, can have appreciable van der Waals contributions that must be accounted for in correlating spectral shifts with heats of acid-base interaction. Although the van der Waals contributions to the spectral shifts may be less important in the case of protons (as in  $-\text{OH}$  and  $-\text{NH}$  groups), these contributions are more appreciable for the heavier elements (such as  $-\text{P=O}$  and  $-\text{C=O}$  groups). Drago et al.<sup>11,28-32</sup> studied proton NMR chemical shifts as a method of predicting strength of acid-base interactions. Three-component systems were used so that the observed shift had no van der Waals contribution and represented only the extent of the acid-base interaction. We have conducted similar NMR studies in three-component systems using the  $^{31}\text{P}$  chemical shift of  $\text{Et}_3\text{PO}$  to predict heats of acid-base interactions. These studies will be reported in a future publication.

It is the purpose of this paper to determine the van der Waals and acid-base contributions to the overall  $^{31}\text{P}$  chemical shifts ( $\Delta\delta^d$  and  $\Delta\delta^{ab}$ ) and to the acceptor numbers ( $\text{AN}^d$  and  $\text{AN}-\text{AN}^d$ ) of the Mayer and Gutmann two-component systems and to illustrate the method with experimental results for 30 test liquids. For each of these 30 liquids, surface tensions and interfacial tensions versus squalane have been determined so that  $\gamma^d$  values could be determined and used to predict the magnitude of the van der Waals contribution to  $\Delta\delta^d$  and to  $\text{AN}^d$ .

## Experimental Section

**Materials.** Aldrich hexane, benzene, methylene iodide, and spectral-grade carbon tetrachloride were dried over freshly activated Linde 4-Å molecular sieves for several weeks prior to use. Pyridine from Fisher was dried over KOH pellets and distilled from BaO. Squalane from Aldrich was stripped of hydrophilic impurities with a basic alumina column. Solvents used for interfacial tension measurements were obtained from Aldrich in high purity and used as received.

Triethylphosphine oxide was prepared by the method of Burg and McKee.<sup>33</sup> The material was sublimed several times at room temperature under high vacuum. The anhydrous white crystalline solid had a melting point of 50–51 °C. Due to the hygroscopic nature of  $\text{Et}_3\text{PO}$  and some of the solvents, all sample preparations, handling, etc., were done in a dry nitrogen glovebag.

**Measurements.** Infrared measurements were made with a Mattson FTIR Sirius 100 spectrometer equipped with a liquid cell with KBr windows. The cell was dried in an oven and loaded in a glovebag purged with dry nitrogen. IR peak transmissions were generally 20–50% with peak centers determined at half-height.

A JEOL FX90Q multinuclear NMR was used for measuring  $^{31}\text{P}$  chemical shifts. Sample tubes were 10 mm in diameter and equipped with a coaxial external reference cell containing diphenylphosphinic chloride. Chemical shifts were determined at several different concen-

**Table II.** Liquid-Squalane Interfacial Tension Measurements (22.5 °C)<sup>a</sup>

liquid	$\gamma$ (mJ/m <sup>2</sup> )	$\gamma_{12}$ (mJ/m <sup>2</sup> )	$\gamma^d$ (mJ/m <sup>2</sup> )
dioxane	33.2		33.2
pyridine	37.0		37.0
hexane	18.2		18.2
benzonitrile	39.1		39.1
benzene	28.6		28.6
tetrahydrofuran	26.5		26.5
carbon tetrachloride	26.8		26.8
diethyl ether	16.9		16.9
ethyl acetate	23.7		23.7
methyl acetate	25.1		25.1
<i>N,N</i> -dimethylacetamide	32.4	4.2 ± 0.1	29.2 ± 0.1
1,2-dichloroethane	32.3		32.3
<i>N,N</i> -dimethylformamide	36.8	6.5 ± 0.1	31.3 ± 0.1
acetone	23.8	1.4 ± 0.03	23.6 ± 0.03
dimethyl sulfoxide	43.5	14.5 ± 0.1	30.0 ± 0.1
dichloromethane	27.6		27.6
nitromethane	37.0	11.8 ± 0.1	26.2 ± 0.1
acetonitrile	29.0	8.5 ± 0.1	21.9 ± 0.1
chloroform	27.1		27.1
<i>tert</i> -butyl alcohol	20.2		20.2
isopropyl alcohol	21.2		21.2
<i>n</i> -butyl alcohol	25.2		25.2
formamide	57.3	29.5 ± 0.5	28.8 ± 0.5
ethanol	22.2	2.6 ± 0.1	21.1 ± 0.1
methanol	22.3	6.3 ± 0.1	18.1 ± 0.1
acetic acid	27.4	5.3 ± 0.1	23.3 ± 0.1
water	72.6	52.3 ± 0.1	21.7 ± 0.1
2,2,2-trifluoroethanol	21.5	10.4 ± 0.1	14.4 ± 0.1
hexafluoro-2-propanol	17.6	10.2 ± 0.4	11.9 ± 0.4
trifluoroacetic acid	13.8	8.7 ± 0.1	10.5 ± 0.1

<sup>a</sup> Surface tensions from J. J. Jasper's tables,<sup>39</sup> except for squalane and *N,N*-dimethylformamide. These two surface tensions and all interfacial tensions determined by the drop volume method, corrected by eq 11 of ref 35.

trations, corrected for volume susceptibility differences, and extrapolated to infinite dilution. All  $^{31}\text{P}$  NMR spectra were recorded with proton decoupling to obtain maximum accuracy and sensitivity.

Interfacial tensions were determined at 22.5 °C with the drop volume method.<sup>34,35</sup> A micrometer syringe was used with stainless steel dropping tips of diameters as shown in Table II. Squalane (2,6,10,15,19,23-hexamethyltetracosane), a saturated liquid hydrocarbon, was used as the reference liquid, and interfacial tensions were measured against squalene with the polar organic liquids that were immiscible in squalene. Interfacial tensions were usually measured with the denser (polar) liquid in the syringe, and drops of the polar liquid were dropped downward in the squalene. However, if the denser polar liquid so preferentially wet the stainless steel tip that liquid climbed up the outer wall of the tip as the drop was formed, then the procedure was reversed and drops of squalane were formed upward into the polar liquid. An example is the measurement of the interfacial tension of acetonitrile in squalane, where the acetonitrile crept up the outside of the tip as drops were formed downward into squalane, and the observed drop volume corresponded to an interfacial tension of only 5.8 mJ/m<sup>2</sup>. However, when squalane drops were formed upward into the acetonitrile, drop volumes were larger and corresponded to an interfacial tension of 8.6 mJ/m<sup>2</sup>; the latter value is used in Table II. Polar liquids such as methanol, ethanol, acetone, and water were observed to creep up the dropping tip and to minimize drop size in squalane. Larger drop volumes were observed when squalane drops were formed upward into these polar liquids, and interfacial tensions calculated from these larger volumes are listed in Table II. All drops were formed in mutually saturated liquids. The empirical corrections of Harkins for drop volume measurements of surface and interfacial tension were used.<sup>34,35</sup>

## Results

The  $^{31}\text{P}$  NMR chemical shift  $\Delta\delta$  of  $\text{Et}_3\text{PO}$  dissolved in acidic solvents is composed of two additive contributions, a van der Waals contribution and a Lewis acid-base contribution:

$$\Delta\delta = \Delta\delta^d + \Delta\delta^{ab} \quad (5)$$

$\Delta\delta$  is the total shift of the  $^{31}\text{P}$  NMR peak for  $\text{Et}_3\text{PO}$  from the

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**Table III.** Van der Waals and Acid-Base Contributions to Acceptor Numbers

liquid	$\delta_0^a$	$\Delta\delta = \delta_0 + 7.37$	$\Delta\delta^d = 0.312\gamma^d$	$\Delta\delta^{ab}$	AN	AN <sup>d</sup>	AN-AN <sup>d</sup>	AN* kcal/mol
dioxane	2.92	10.29	10.35	-0.06	10.8	10.9	0.0	0.0
hexane	-1.68	5.69	5.68	-0.01	0.0	0.0	0.0	0.0
benzonitrile	4.93	12.30	12.21	0.09	15.5	15.3	0.2	0.06
pyridine	4.36	11.73	11.54	0.19	14.2	13.7	0.5	0.14
benzene	1.81	9.18	8.93	0.25	8.2	7.6	0.6	0.17
tetrahydrofuran	1.71	9.08	8.27	0.81	8.0	6.1	1.9	0.5
carbon tetrachloride	1.96	9.33	8.36	0.97	8.6	6.3	2.3	0.7
diethyl ether	-0.04	7.33	5.28	2.05	3.9	-1.0	4.9	1.4
ethyl acetate	2.28	9.65	7.41	2.24	9.3	4.0	5.3	1.5
methyl acetate	2.88	10.25	7.83	2.42	10.7	5.0	5.7	1.6
<i>N,N</i> -dimethylacetamide	4.12	11.49	9.05	2.44	13.6	7.9	5.7	1.6
1,2-dichloroethane	5.43	12.80	10.07	2.73	16.7	10.3	6.4	1.8
<i>N,N</i> -dimethylformamide	5.14	12.51	9.70	2.81	16.0	9.4	6.6	1.9
acetone	3.65	11.02	7.32	3.70	12.5	3.8	8.7	2.5
dimethyl sulfoxide	6.54	13.91	9.30	4.61	19.3	8.5	10.8	3.1
dichloromethane	6.99	14.36	8.61	5.75	20.4	6.9	13.5	3.9
nitromethane	7.05	14.42	8.12	6.30	20.5	5.7	14.8	4.3
acetonitrile	6.37	13.74	6.79	6.95	18.9	2.6	16.3	4.7
chloroform	9.01	16.38	8.40	7.98	25.1	6.4	18.7	5.4
<i>tert</i> -butyl alcohol	9.86	17.23	6.31	10.92	27.1	0.6	26.5	7.6
2-propanol	12.63	20.00	6.59	13.43	33.6	2.1	31.5	9.1
<i>n</i> -butyl alcohol	13.99	21.36	7.86	13.50	36.8	5.1	31.7	9.1
formamide	15.27	22.64	8.93	13.71	39.8	7.6	32.2	9.3
ethanol	14.46	21.83	6.54	15.29	37.9	2.0	35.9	10.3
methanol	15.99	23.36	5.61	17.75	41.5	-0.2	41.7	12.0
acetic acid	20.85	28.20	7.22	20.98	52.9	3.6	49.3	14.2
water	21.66	29.04	6.73	22.31	54.8	2.4	52.4	15.1
trifluoroethanol	21.02	28.39	4.46	23.93	53.3	-2.9	56.2	16.2
hexafluoro-2-propanol	24.56	31.93	3.69	28.24	61.6	-4.7	66.3	19.1
trifluoroacetic acid	43.17	50.52	3.26	47.26	105.3	-5.7	111.0	31.9

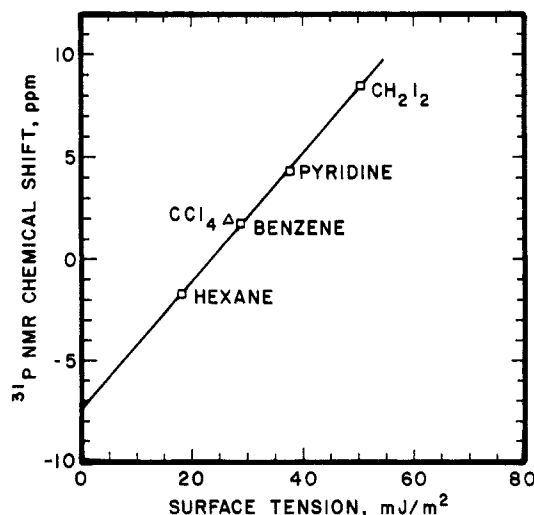
<sup>a</sup> Data from refs 24 and 27. Values are determined at infinite dilution and include volume susceptibility corrections.

position of the vapor peak, as determined by extrapolation from measured values in neutral (or nonacidic) liquids as a function of their surface tension, as shown in Figure 1. In Figure 1 and in the first column of Table III the NMR peak positions are all referenced to the external standard, diphenylphosphinic chloride, and are all extrapolated to infinite dilution and corrected for volume susceptibility differences compared to *n*-hexane, as done by Mayer and Gutmann. Although only the acid-base contribution is important in characterizing electron-acceptor (or electrophilic) properties, it is necessary to determine  $\Delta\delta^d$  in order to obtain  $\Delta\delta^{ab}$ .

**Relation of NMR Shifts to  $\gamma^d$  Energies of Nonacidic Test Liquids.** In order to determine the van der Waals contribution to the  $^{31}\text{P}$  NMR chemical shift of  $\text{Et}_3\text{PO}$  in an electrophilic medium, it was first necessary to determine the  $^{31}\text{P}$  NMR chemical shift of  $\text{Et}_3\text{PO}$  in test liquids that have no electrophilic properties and interact with  $\text{Et}_3\text{PO}$  only by van der Waals interactions and to determine the relation of the  $^{31}\text{P}$  NMR shifts to the  $\gamma^d$  of such test liquids. For these liquids the surface tension  $\gamma$  and the van der Waals contribution to surface tension  $\gamma^d$  are considered equal. The liquids selected had a broad range of surface tensions; none were acidic, and none were sufficiently self-associated acid-base complexes to be immiscible in squalane. The liquids used were hexane ( $\gamma = 18.4 \text{ mJ/m}^2$ ), benzene ( $\gamma = 28.9 \text{ mJ/m}^2$ ), pyridine ( $\gamma = 38.0 \text{ mJ/m}^2$ ), and methylene iodide ( $\gamma = 50.8 \text{ mJ/m}^2$ ). The correlation between the  $^{31}\text{P}$  NMR chemical shift  $\Delta\delta^d$  and the van der Waals contribution to surface tension is illustrated in Table I and Figure 1 and expressed mathematically from linear regression to be

$$\Delta\delta^d = 0.312\gamma^d = 7.37 + \delta_0 \quad (6)$$

Table I and Figures 1 and 2 also include carbon tetrachloride ( $\gamma = 27.0 \text{ mJ/m}^2$ ), as a test liquid, for it has often been considered to be a neutral liquid. However, as can be seen in both figures, the infrared and the NMR shifts for  $\text{Et}_3\text{PO}$  in carbon tetrachloride are always a little greater than can be attributed to the van der Waals interactions and must be attributed to the weak acidity of carbon tetrachloride, as is illustrated in the AN-AN<sup>d</sup> results of Table III.



**Figure 1.** Chemical shifts for the  $^{31}\text{P}$  NMR peak of  $\text{Et}_3\text{PO}$  due to van der Waals interactions in nonacidic solvents covering a wide range of surface tensions.

There is an exception to the linear relation of  $\Delta\delta^d$  and of  $\Delta\delta^d$  to  $\gamma^d$  illustrated in Figures 1 and 2 for the saturated ring compounds (cyclohexane, *cis*-decahydronaphthalene, *trans*-decahydronaphthalene). The  $\Delta\delta^d$  and of  $\Delta\delta^d$  shifts for these hydrocarbons are also a linear function of  $\gamma^d$ , but with smaller slope; the two lines intersect at the values for pentane and hexane.

**Surface Free Energies of Polar (Squalane-Immiscible) Liquids.** In evaluating liquids having both van der Waals and Lewis acid-base interactions with the test probe  $\text{Et}_3\text{PO}$ , it is necessary to determine the van der Waals contribution to surface free energy ( $\gamma^d$ ), from which the  $\Delta\delta^d$  component could be determined with eq 6. The van der Waals contribution to surface tension ( $\gamma^d$ ) was obtained for each acidic test liquid by measuring the interfacial tension between the test liquid and a reference hydrocarbon liquid having only van der Waals interactions. Squalane (2,6,10,15,19,23-hexamethyltetracosane), a liquid saturated hy-

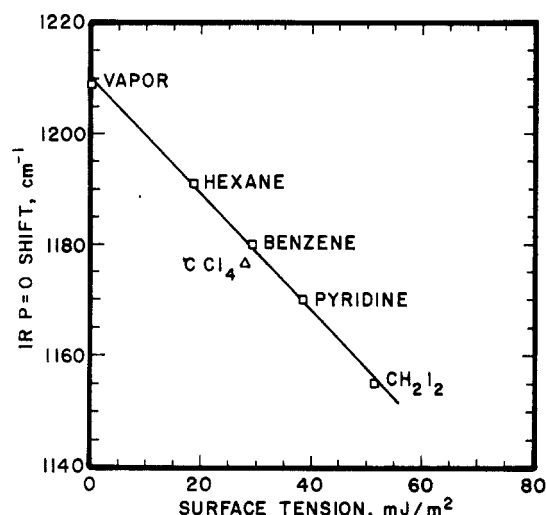


Figure 2. Chemical shifts for the  $\text{P}=\text{O}$  infrared stretch frequency of  $\text{Et}_3\text{PO}$  in nonacidic solvents covering a wide range of surface tensions.

drocarbon, was chosen as the reference van der Waals liquid because it has no acidic or basic sites, and its large molar volume minimizes the solvency for polar organic liquids such as acetone and ethanol. It was also expected that the six methyl side groups would interrupt the mutual attraction of parallel oriented chains so as to minimize the correlated molecular orientation (CMO) interaction of long-chain alkanes that provides an incremental increase in surface tension.<sup>36,37</sup> The methyl groups do indeed minimize interchain attractions enough for this 24-carbon alkane to be liquid at room temperature, but not enough to completely eliminate the CMO contribution to surface tension. The interfacial tension of squalane against water was used as the standard for determining  $\gamma^d$  for squalane, with 21.7 mJ/m<sup>2</sup> for the  $\gamma^d$  of water at 22.5 °C;<sup>38</sup> the result is that the  $\gamma^d$  for squalane is 28.4 mJ/m<sup>2</sup>, though its surface tension is 29.4 mJ/m<sup>2</sup>. The values of  $\gamma_2^d$  for the squalane-immiscible polar liquids were determined from their interfacial tensions against squalane with eq 1. Test liquids soluble in squalane have negligible acid-base self-association; for these liquids  $\gamma = \gamma^d$ . All surface and interfacial tension results are shown in Table II.

**Contributions to NMR Shifts and Acceptor Numbers.** Once values of  $\gamma_2^d$  are determined,  $\Delta\delta^d$  and  $\Delta\delta^{ab}$  contributions to the  $^{31}\text{P}$  shifts ( $\delta$ ) of  $\text{Et}_3\text{PO}$  and to AN values were calculated from

$$\text{AN}^d = (100/42.59 \text{ ppm})(\Delta\delta - \Delta\delta_{\text{hex}}) = 2.348(\Delta\delta - \Delta\delta_{\text{hex}}) \quad (7)$$

$$\text{AN} - \text{AN}^d = 2.348(\Delta\delta - \Delta\delta^d) = 2.348(\delta_0 + 7.37 - 0.312\gamma^d) \quad (8)$$

$\text{AN}^d$  is the van der Waals contribution to the acceptor numbers, referenced to *n*-hexane.  $\text{AN}^d$  is zero for *n*-hexane, and positive for liquids with greater  $\gamma^d$ -values. Table III lists the  $^{31}\text{P}$  NMR peak positions ( $\delta_0$ ) for  $\text{Et}_3\text{PO}$  (referenced to diphenylphosphinic chloride, extrapolated to zero concentration, and corrected for volume susceptibility vs *n*-hexane) for 30 liquids, the total chemical shifts ( $\Delta\delta$ ), the van der Waals and acid-base contributions to the NMR shifts ( $\Delta\delta^d$  and  $\Delta\delta^{ab}$ ), and to the acceptor numbers ( $\text{AN}^d$  and  $\text{AN} - \text{AN}^d$ ). It also introduces  $\text{AN}^*$ , proportional to  $\text{AN} - \text{AN}^d$ , with units of kilocalories per mole for the acid-base interaction of the test liquid with  $\text{Et}_3\text{PO}$ .

**Van der Waals Contributions to Infrared Shifts,  $\Delta\nu^d_{\text{PO}}$ .** When  $\text{Et}_3\text{PO}$  interacts with solvents, frequency shifts are also observed for the infrared peak of the  $\text{P}=\text{O}$  stretch. These infrared shifts

are also composed of a van der Waals and a Lewis acid-base contribution, as in eq 4.

Spectral shift studies have previously been reported regarding van der Waals and acid-base contributions to infrared shifts.<sup>23</sup> The infrared carbonyl shift of ethyl acetate in nonacidic liquids was found to be related to the van der Waals contribution to surface tension,  $\gamma^d$ , and to the van der Waals contribution to the cohesive energy density ( $\text{CED}^d$ ) by the following expressions:

$$\Delta\nu^d_{\text{CO}} = -0.714\gamma^d \quad (9)$$

$$\Delta\nu^d_{\text{CO}} = -0.247\text{CED}^d \quad (10)$$

A similar approach was taken to study the infrared  $\text{P}=\text{O}$  shift of  $\text{Et}_3\text{PO}$ . Liquids were selected that would not self-associate (that is,  $\gamma^d = \gamma$ ) nor contribute to an acid-base interaction with  $\text{Et}_3\text{PO}$ . Dilute solutions ( $\sim 0.05 \text{ M}$ ) of  $\text{Et}_3\text{PO}$  in hexane, benzene, pyridine, and methylene iodide were prepared, and the infrared peak position of the  $\text{P}=\text{O}$  stretching frequency absorption was determined, as shown in Table I and Figure 2 and as summarized by eq 11.

$$\nu^d_{\text{PO}} = 1209.9 - 1.06\gamma^d \quad (11)$$

## Discussion

The interaction energies of molecules interacting with their immediate neighbors have two major contributions: van der Waals interactions (mainly dispersion force interactions) and Lewis acid-base interactions (including hydrogen bonds). The van der Waals contributions provide endothermic heats of mixing and tend to diminish solubility, as demonstrated by Hildebrand's cohesive energy density approach.<sup>13</sup> In contrast, Lewis acid-base interactions between solvent and solute provide exothermic heats of mixing and enhance solubility. In three-component systems (acid, base, solvent) the van der Waals contributions depend on the major component (the solvent) and do not change upon complexation of the acid and base;<sup>11</sup> in such systems the calorimetric heats of interaction and the spectral shifts result solely from Lewis acid-base interactions. In two-component systems (acid and base only) such as those studied by Mayer and Gutmann, both van der Waals and Lewis acid-base contributions must be taken into account. The IR and NMR shifts reflect the sum of the two contributions, but it is only the acid-base contribution to these shifts that can be used to determine the acid-base contribution to the heat of mixing.

In the Mayer/Gutmann two-component systems, the acidic solvent is present in large excess, which is a cause of two additional complications: (1) many acidic solvents also have basic sites and at higher concentrations tend to form self-associated acid-base complexes and (2) at the higher ratios of acid to base 2:1 complexes are sometimes favored. Both considerations complicate the interpretation of the chemical shifts and acceptor numbers in terms of acid-base interactions. In a future publication we will report the results of our  $^{31}\text{P}$  NMR chemical shift studies carried out in neutral solvents where van der Waals shifts, self-association of the test acids, and 2:1 adduct formation are avoided.

**Acceptor Numbers.** Mayer and Gutmann<sup>12</sup> stated that "in principle, all solvents are amphoteric, i.e., they may act as nucleophiles and electrophiles simultaneously". Our current calorimetric studies of heats of mixing tend to support this view; certainly solvents strongly enough self-associated to be immiscible in squalane do indeed act simultaneously as acids and bases, forming acid-base complexes. Mayer and Gutmann characterized the nucleophilic properties of liquids with the donor number (DN) concept that was defined as "the negative  $\Delta H$  value for the 1:1 adduct formation between  $\text{SbCl}_5$  and the (test liquid) molecules in a dilute solution of 1,2-dichloroethane". These tests were conducted in a three-component system where the van der Waals contribution canceled out, making the interaction essentially an acid-base interaction. They further stated that "unfortunately no analogous quantity could be defined for characterizing the electrophilic properties of solvents". As an alternative they used the  $^{31}\text{P}$  NMR chemical shift of  $\text{Et}_3\text{PO}$  in a candidate liquid (a two-component system) to develop a relative measure of acid strength. The magnitude of this NMR shift was used to calculate

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an acceptor number for the solvent from the following equation

$$AN = 100(\delta_{\text{corr}})/\delta_{\text{corr}}(\text{SbCl}_5\text{-Et}_3\text{PO}) \quad (12)$$

where  $\delta_{\text{corr}}$  is the  $^{31}\text{P}$  NMR chemical shift of  $\text{Et}_3\text{PO}$  at infinite dilution in a solvent S. This chemical shift value is referenced to an infinitely dilute solution of  $\text{Et}_3\text{PO}$  in *n*-hexane and corrected for difference in volume susceptibilities between solvent S and *n*-hexane. Thus, for *n*-hexane  $\delta_{\text{corr}} = 0$ , but the measured value with respect to the external standard (after extrapolation to infinite dilution and correction for volume susceptibility differences) is  $-1.68$  ppm, as shown in column 1 of Table III. The denominator of eq 12 denotes the corresponding chemical shift value for the adduct  $\text{SbCl}_5\text{-Et}_3\text{PO}$  at infinite dilution in 1,2-dichloroethane, which is arbitrarily assigned an AN value of 100. Liquids with the higher acceptor numbers were considered to be more acidic.

Mayer and Gutmann chose hexane as a standard solvent, and any solvent in which the  $^{31}\text{P}$  NMR shift for  $\text{Et}_3\text{PO}$  exceeded that observed in hexane was assigned an acceptor number. Thus, in principle, all saturated hydrocarbons above hexane would have AN values, and aromatic hydrocarbons were assigned larger AN values. Even appreciably basic liquids without electrophilic sites sufficient to promote self-association (and immiscibility in squalane), such as diethyl ether, tetrahydrofuran, dioxane, and pyridine, were assigned appreciable AN values. Such AN values have been difficult for experimentalists to accept, but the AN-AN<sup>d</sup> values of Table III agree with laboratory experience.

It should be noted that the AN of 100 assigned to dilute solutions of antimony pentachloride in 1,2-dichloroethane is calculated from a  $\delta_{\text{corr}}$   $^{31}\text{P}$  NMR shift for  $\text{Et}_3\text{PO}$  of 42.59 ppm referenced to  $\text{Et}_3\text{PO}$  solutions in *n*-hexane, so the total shift will include a van der Waals contribution of 5.69 ppm for hexane minus a 10.07 ppm van der Waals contribution for 1,2-dichloroethane, as shown in Table III. Thus, the acid-base contribution to this shift  $\Delta\delta^{\text{ab}}$  is 38.21 ppm. Should we now use the shift of 38.21

ppm for the standard? If the values of acceptor numbers are to be changed to measure only acidity, perhaps it would be better to use units of kilocalories per mole, for as will be shown in paper 2 of this series, the acid-base contributions to the  $^{31}\text{P}$  NMR shifts of  $\text{Et}_3\text{PO}$  are directly proportional to the heats of acid-base interaction of  $\text{Et}_3\text{PO}$  with acidic liquids, and then the new AN values (AN\*) would be in the same units as DN values. With the use of  $-25.8$  kcal/mol as the heat of acid-base interaction of  $\text{Et}_3\text{PO}$  with antimony pentachloride (the negative of the DN for  $\text{Et}_3\text{PO}$ ) to correspond to the 38.21 ppm acid-base contribution to the NMR shift,

$$AN^* = 25.8(AN-AN^d)/(38.21 \times 2.348) = 0.288(AN-AN^d) \quad (13)$$

Values of AN\* (in kilocalories per mole) are listed in Table III.

### Conclusions

The experimental results in this study show that the van der Waals contribution to the  $^{31}\text{P}$  NMR chemical shifts of  $\text{Et}_3\text{PO}$  are quite significant, as are also the infrared chemical shifts for the  $\text{-P=O}$  stretching peaks. When the  $^{31}\text{P}$  NMR shifts are corrected by subtracting the van der Waals contribution, the resulting shifts ( $\Delta\delta^{\text{ab}}$ ) and the corrected acceptor numbers AN-AN<sup>d</sup> or of AN\* (in kcal/mol) appear to be more reasonable, for only acids are found to have appreciable values of AN-AN<sup>d</sup> or of AN\*.

**Acknowledgment.** We acknowledge the support of this research by the Department of Energy (Grant No. DE-FG22-87PC9925) and by IBM (San Jose). Appreciation is expressed to Dr. T. B. Lloyd and to Prof. James E. Roberts for helpful discussions and contributions to this effort and to W. E. Pastore for the interfacial tension measurements.

Registry No.  $\text{Et}_3\text{PO}$ , 597-50-2.

## Natural-Abundance Two-Dimensional Solid-State $^{29}\text{Si}$ NMR Investigations of Three-Dimensional Lattice Connectivities in Zeolite Structures

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**Abstract:** The 3D lattice connectivities in zeolites ZSM-12 and KZ-2 have been investigated by natural-abundance  $^{29}\text{Si}/^{29}\text{Si}$  COSY and INADEQUATE 2D NMR experiments. In both cases the results are in exact agreement with the lattice structures, the INADEQUATE experiment being particularly successful and detecting all of the connectivities. In addition, it is possible to observe directly the scalar *J* couplings that are in the range of 10–15 Hz. The approach is of quite general applicability and may be extended to other 3D structures.

Zeolites are porous aluminosilicates (tectosilicates) whose unique 3D tetrahedral framework structures incorporate cavities and interconnecting channel systems,<sup>1</sup> giving them a size and shape selectivity for sorbed organic molecules that makes them of considerable importance in industry as molecular sieves and as catalysts.<sup>2</sup> Although they are highly crystalline and their structures are often highly symmetrical, there are difficulties in determining their crystal structures by diffraction techniques. First, they are usually microcrystalline with particle dimensions of only a few micrometers, which precludes the simple application of single-crystal diffraction techniques, and recourse must be made to much more limited power diffraction data.<sup>3</sup> Second, Si and

Al atoms have very similar scattering factors and, in addition, are often disordered within the framework of the zeolite so that even when the topology of the overall crystal structure can be

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