

excess base. The purity of the sample was calculated from the moles of sodium hydroxide consumed in the hydrolysis.

Anal. Calcd. for C_4H_7ON : C, 56.44; H, 8.30; N, 16.46. Found: C, 56.51; H, 8.42; N, 16.44.

Apparatus.—The freezing points were determined in a conventional apparatus which is described elsewhere.³ The temperatures were measured with a ten-junction, calibrated thermopile⁴ and were recorded automatically. Calibration of the thermopile itself⁵ and calibration of the thermopile and recording device at the freezing point of triple-distilled mercury indicate that the instrument is accurate to about 0.03°. Actual freezing points of aqueous pyrrolidone solutions given in Table I are accurate to $\pm 0.1^\circ$ and the extrapolated eutectic points (Fig. 1) are estimated to be accurate to $\pm 1^\circ$. The freezing points of 2-pyrrolidone and pyrrolidone monohydrate are estimated to be accurate to $\pm 0.1^\circ$.

2-Pyrrolidone-Water Solutions.—The various solutions were made by weighing to the nearest milligram the 2-pyrrolidone and the water. Approximately 50 ml. of the known solution was transferred to the cell for the freezing point determination. The freezing points and mole % H_2O of the various solutions are given in Table I and a plot of the data is shown in Fig. 1.

TABLE I

FREEZING POINTS OF AQUEOUS PYRROLIDONE SOLUTIONS			
F.p., °C.	Mole % H_2O	F.p., °C.	Mole % H_2O
25.57	0.0	20.3	71.3
22.8	4.6	16.0	74.4
20.0	9.1	12.6	76.9
17.6	13.0	8.8	78.9
15.2	16.7	- 0.5	83.1
13.9	18.5	- 8.5	85.7
13.1	21.7	-12.4	86.4
19.5	27.2	-13.7	86.9
25.4	34.0	-12.8	88.5
28.4	39.9	- 9.1	91.4
30.4	48.1	- 4.4	95.5
30.3	52.8	- 2.0	98.0
26.9	62.9	- 0.5	99.6
24.7	66.5	0.0	100.0

Discussion

The phase diagram (Fig. 1) shows that 2-pyrrolidone and water form only a monohydrate confirming the work of Tafel and Stern.² The freezing point of the monohydrate is 30.4° , and the eutectic points of the phase system are estimated to be 12 and -14° .

Acknowledgment.—I am indebted to Dr. L. T. Hallett who encouraged me to undertake this study and to Mr. R. C. Rheinart who made the solutions and determined their freezing points.

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PROTON NUCLEAR RESONANCE SPECTROSCOPY. I. RELIABLE SHIELDING VALUES BY "INTERNAL REFERENCING" WITH TETRAMETHYLSILANE

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Tetramethylsilane, a highly soluble volatile liquid

which is magnetically isotropic, non-associative and chemically unreactive, appears particularly suitable as a homogeneous "internal reference" for proton nuclear spin resonance (n.s.r.) spectroscopy. Its sharp peak falls beyond the usual spectral region (more shielded) and is readily identified. Shielding values ("chemical shifts") so measured in CCl_4 solution are highly reproducible, are commonly independent of temperature or concentration and agree closely with the most precise and reliable published "externally referenced" measurements, the latter having been obtained by extrapolation to infinite dilution in CCl_4 .^{1,2} In Table I the equivalence of the two techniques is made clear.³

TABLE I

A DEMONSTRATION OF THE EQUIVALENCE OF "SINGLE PHASE" AND "EXTRAPOLATED TWO PHASE" REFERENCE TECHNIQUES FOR THE PRECISE MEASUREMENT OF THE PROTON NUCLEAR RESONANCE SHIELDING VALUE, τ^b

Compound	"Extrapolated two-phase" ^a τ (p.p.m.) ^b	"Single-phase" ^c τ (p.p.m.) ^b	Vol. % concn. in CCl_4
Benzene	2.74 ^c	2.734 $\pm$ 0.003	2.0
$C_6H_5C_2H_5$	2.89 ^c	2.888 $\pm$.002	5
$(C_6H_5CH_2)_2$	2.89 ^c	2.893 $\pm$.001	5
$p-C_6H_4(CH_3)_2$	3.05 ^c	3.053 $\pm$.003	5
Cyclooctatetraene	4.26 ^c	4.309 $\pm$.004	3.0
CH_3NO_2	5.69 ^d	5.720 $\pm$.002	2.0
$C_6H_5OCH_3$	6.31 ^d	6.266 $\pm$.002	6.0
CH_3OH	6.60 ^d	6.622 $\pm$.002	1.0
$(C_6H_5CH_2)_2$	7.13 ^c	7.129 $\pm$.001	5
$C_6H_5CH_2CH_3$	7.42 ^c	7.382 $\pm$.003	5
$C_6H_5CH_3$	7.67 ^d	7.663 $\pm$.003	2.0
Acetic anhydride	7.81 ^d	7.809 $\pm$.003	3.0
Methyl iodide	7.81 ^d	7.843 $\pm$.004	2.0
Acetone	7.91 ^c	7.915 $\pm$.003	3.0
CH_3CO_2H	7.90 ^d	7.930 $\pm$.004	6.0
Acetonitrile	8.10 ^d	8.026 $\pm$.002	3.0
Cyclohexane	8.51 ^c	8.564 $\pm$.002	1.0

^a Shielding-value measurements made at two or more concentrations in CCl_4 are extrapolated to zero concentration. By this procedure the magnetic susceptibility correction is rendered constant. ^b τ (in p.p.m.) = $[10,000 - 10^6 (\nu_{obs.} - \nu_{Me_4Si}) / \nu_{Me_4Si}] = [10,000 - 10^6 (H_{Me_4Si} - H_{obs.}) / H_{Me_4Si}]$. Increasing values of τ signify increasing shielding of the proton. Error values are standard deviations for the measurements. ^c Data of ref. 1, converted to τ -values by sign reversal and addition of 5.24 p.p.m.; error (standard deviation) is ± 0.033 p.p.m. for eight remeasured values. ^d Data of ref. 2, expressed in p.p.m. (40.00 mc./sec. frequency assumed) and converted to τ -values by addition of 5.21 p.p.m.; error (standard deviation) is ± 0.036 p.p.m. for nine remeasured values.

Conventional n.s.r. equipment was employed, namely, a Varian V-4300-2 40.00 mc./sec. spectrometer with flux stabilizer, sample spinner, audio-oscillator, Hewlett-Packard 522-B frequency counter, and Varian recorder. Sample solutions ($1/2$ ml.) containing 1 vol. % Me_4Si (pure grade, Anderson Laboratories, Inc., Weston, Mich.) were sealed in ordinary 5 mm. o.d. "Pyrex" tubes. The sweep was such that 1.0 p.p.m. occupied approx. 100 mm. of chart; peak positions were measured to the nearest tenth of a mm.

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(2) A. L. Allred and E. G. Rochow, *ibid.*, **79**, 5361 (1957).

(3) For highest reproducibility, shielding value measurements referenced externally by H_2O must be corrected for temperature, about 0.005 p.p.m. being added per 1° rise. Measurements such as those of refs. 1 and 2, if made at 23.0° , are converted to τ -values by addition of 5.207 p.p.m.

relative to "side-band" peaks produced in the recorded spectrum by the audio-oscillator. The frequency separation of the "side-band" from its "parent-peak" was obtained, by direct counting, to ± 0.05 c.p.s. The "side-band" from the Me_4Si "parent-peak" thus may be brought very close to the "parent-peak" of the compound under study (or *vice versa*); a separation of 0.3 to 0.5 p.p.m. is convenient. The novel feature of this technique, not previously described, is that after sweeping through a Me_4Si "side-band" and then through the "parent-peak" of the compound, the "side-band" frequency can be changed suddenly to a new value such that a new "side-band" peak is produced in the *same sweep* but on the *other side* of the compound "parent-peak." The peak position is then obtained by simple interpolation between two such Me_4Si "side-band" peaks which are separated by *ca.* 1 p.p.m. Each τ -value reported in this communication is the average of four to twelve interpolations, the sweep direction being routinely alternated to preclude directed error.

Internally referenced measurements made on binary mixtures or on very concentrated solutions appear to be only slightly less reliable.⁴ Shielding values so obtained for seventeen sharp peaks⁴ were remeasured in dilute CCl_4 solution to ± 0.003 by the present technique. The reported values⁴ were found to average 0.024 p.p.m. low, with a standard deviation of ± 0.045 .

In the present research several of the compounds of Table I were re-examined as pure liquids, to which 3% by volume of Me_4Si had been added to provide the internal reference. The values for τ so measured were: CH_3OH , 6.653 ± 0.004 ; acetone, 7.909 ± 0.003 ; $\text{CH}_3\text{CO}_2\text{H}$, 7.934 ± 0.004 ; CH_3CN , 8.033 ± 0.004 ; cyclohexane, 8.544 ± 0.004 ; C_6H_6 , 2.841 ± 0.004 . In the last-mentioned case the τ -value is significantly higher than that of Table I; such specific medium effects are encountered when aromatic molecules are present in high concentration.⁵ Pure nitromethane so studied had $\tau = 5.640 \pm 0.002$, the displacement toward lower shielding being attributable to weak hydrogen-bonding; similar effects have been noted for chloroform.^{6,7}

Internal referencing is particularly suitable⁸ for the study of weak solvent effects, since external referencing requires the making of highly precise magnetic susceptibility corrections; volume susceptibilities are not usually known with the needed accuracy,⁵⁻⁷ and even when known require an empirical proportionality constant rather than the theoretically-predicted one.⁵ Temperature corrections³ do not appear to be required for measurements referenced internally; for $(\text{C}_6\text{H}_5\text{CH}_2)_2$, upon

20° elevation of temperature, $\tau(\text{CH}_2)$ was found to be 7.127 ± 0.006 .

The significant advantages of the tetramethylsilane internal referencing technique are enumerated below.

(1) Reliable, temperature-independent τ -values are obtained from a single sample; extrapolation to infinite dilution is not required.

(2) The τ -value definition of spectral position is simple, precise and operational, and is independent of field strength.

(3) The τ -values are positive in sign for virtually all non-acidic protons, and are not complicated by conflicting definitions.^{2,4}

(4) Special sample cells are unnecessary.

(5) The tetramethylsilane reference peak lies outside the usual spectral region and is readily identified.

(6) With good precision, τ -values can be obtained in any solvent, or in the absence of solvent (exception: Me_4Si is insoluble in D_2O).

(7) Other precise measurements^{1,2,4} are readily converted to τ -values.³

(8) Even very small differences in τ -value (*ca.* 0.01 p.p.m.) can be established accurately; examples include distant-group effects and complex formation.

Unfortunately, several recent and otherwise excellent papers have employed unreliable or non-convertible systems of shielding values.⁸⁻¹¹ Such measurements, even though made with great care, cannot be used satisfactorily as reliable shielding values.

An important conclusion to be drawn is that all subsequently reported proton n.s.r. data *should and can easily* be presented in a truly interconvertible system of units; the author prefers τ -values but welcomes data such as those of refs. 1, 2 and 4.

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