[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF LOYOLA UNIVERSITY]

# Liquid–Liquid Solubility and Vapor Pressure of Heptacosafluorotributylamine[1,2]

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Liquid–liquid solubility curves were obtained for binary mixtures of heptocosafluorotributylamine, $(C_4F_9)_3N$, with methylcyclohexane, *n*-hexane and isoöctane (2,2,4-trimethylpentane). Their critical solution temperatures were found to be 98.4, 60.6 and 53.7°, respectively. Comparison of experimental results with those predicted from the theory of regular solutions reveals the inadequacy of the theory in dealing with these fluorocarbon–hydrocarbon pairs. The anomalous behavior of these liquid pairs is, however, the same as observed previously by Hildebrand and others for other fluorocarbon–hydrocarbon systems. The solubility parameter of 4.6 for $(C_4F_9)_3N$, calculated from a new miscibility equation, is significantly below its value of 5.9 calculated from vapor pressure data and below its value of 5.7 obtained by McLaughlin and Scott from the solubility of iodine and stannic iodide. It is in agreement with the value of 4.8 obtained by the latter two investigators from the solubility of phenanthrene. The anomalous behavior of our liquid pairs is attributed in the main to the hydrocarbons. The measured vapor pressures of $(C_4F_9)_3N$ were: 25.05°, 0.552 ± 0.001 mm.; 45.00°, 2.371 ± 0.015 mm.

## Introduction

The unusual solvent behavior of the fluorocarbon liquids has been extensively studied in the last few years. The conclusion of Scott[3] in 1948 that the abnormally low solubilities of the fluorocarbons in the usual organic solvents could be explained satisfactorily in terms of their low "solubility parameters," $\delta$, or "cohesive energy densities," in the framework of the regular solution theory for non-electrolytes, has since been given added support. The amazingly low solubility of iodine in *n*-perfluoroheptane at 25°, an extreme test of theory, was satisfactorily explained.[4] Further the liquid–liquid solubility of perfluoromethylcyclohexane with benzene, carbon tetrachloride, chlorobenzene, chloroform and toluene,[5] and that of *n*-perfluoroheptane with benzene, carbon tetrachloride and chloroform[6] have been interpreted by Hildebrand to be in accord with the regular solution theory.

There have been cases, however, in which discrepancies with the theory have been observed. Hildebrand first pointed out[6] the disagreements between experiment and theory for the liquid–liquid solubility cases of *n*-perfluoroheptane with isoöctane (2,2,4-trimethylpentane) and *n*-heptane. The latter two solvents behaved as if their solubility-parameter values were much higher than those calculated from their heats of vaporization.[7] Stated otherwise, these hydrocarbons are poorer solvents for the fluorocarbons and better solvents for iodine and phosphorus[8] than might be inferred from their heats of vaporization. Since then other cases[9–14] of fluorocarbon–hydrocarbon solubilities have been investigated for which abnormally low mutual solubilities have been found and for which the solubility parameters of the hydrocarbons were in disagreement with the values calculated from the heats of vaporization.

A number of perfluoro tertiary amines have been prepared in recent years[15] and one of these, heptacosafluorotributylamine, $(C_4F_9)_3N$, has become commercially available.[16] These perfluoroamines are remarkably inert; they exhibit no basic properties. They form no salts with acids and do not react with oxidizing or reducing agents. Their viscosities and surface tensions are low and similar to those for other perfluoro substances. The dielectric constants are so low (about 1.9) that their dipole moments must be practically zero. Thus one may expect the solvent behavior of these perfluoro tertiary amines to be similar to that for the other fluorocarbons studied. Recently McLaughlin and Scott[14] have determined the solubility parameter value for $(C_4F_9)_3N$ as 5.7 from the solubilities of two standard solutes, iodine and stannic iodide. Their study of the solubility of phenanthrene in this fluorocarbon, however, yielded a solubility parameter value of 4.7 for $(C_4F_9)_3N$. These authors pointed out how the regular solution theory did explain the greater part of the non-ideality even in this latter case.

The extremely low internal pressures of the fluorocarbons make possible the study of their miscibilities with other solvents in a convenient temperature range (0 to 150°). We chose to investigate the liquid–liquid solubility of $(C_4F_9)_3N$ with some common organic solvents for two reasons: (1) to obtain new solubility information for this new compound, and (2) to determine whether the results obtained for the various liquid pairs could be explained in terms of the regular solution theory.

## Results

We have determined the critical solution temperatures of $(C_4F_9)_3N$ with methylcyclohexane, 98.4°; *n*-hexane, 60.6°; and isoöctane (2,2,4-trimethylpentane), 53.7°. The miscibility curves are shown in Fig. 1, where the temperature is plotted

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[1] Presented at the 124th Meeting of the American Chemical Society, Chicago, Illinois, September, 1953.

[2] This work was supported by a research grant from Research Corporation.

[3] R. L. Scott, THIS JOURNAL, **70**, 4090 (1948).

[4] H. A. Benesi and J. H. Hildebrand, *ibid.*, **70**, 3978 (1948).

[5] J. H. Hildebrand and D. R. F. Cochran, *ibid.*, **71**, 22 (1949).

[6] J. H. Hildebrand, B. B. Fisher and H. A. Benesi, *ibid.*, **72**, 4348 (1950).

[7] For a review of the various methods of obtaining the solubility parameter see J. H. Hildebrand and R. L. Scott, "Solubility of Non-Electrolytes," Reinhold Publ. Corp., New York, N. Y., 1950, Chap. XXIII.

[8] C. Groot and J. H. Hildebrand, THIS JOURNAL, **70**, 3815 (1948).

[9] J. H. Simons and R. D. Dunlap, *J. Chem. Phys.*, **18**, 335 (1950).

[10] J. H. Simons and J. W. Mausteller, *ibid.*, **20**, 1516 (1952).

[11] J. H. Simons and M. J. Linevsky, THIS JOURNAL, **74**, 4750 (1952).

[12] R. D. Dunlap, R. Digman and J. Vreeland, Abstracts of Papers, 124th Meeting, American Chemical Society, Chicago, Ill., Sept., 1953, p. 16M.

[13] R. D. Dunlap and D. Smyth, *ibid.*, p. 16M-17M.

[14] E. P. McLaughlin and R. L. Scott, "Solubilities of Standard Solid Solutes in Fluorochemicals" (to be published)—the case of phenanthrene in $(C_4F_9)_3N$ and $C_8F_{16}O$.

[15] R. N. Haszeldine, *J. Chem. Soc.*, (*London*), 1638 (1950); 102 (1951); J. H. Simons, *et al.*, *J. Electrochem. Soc.*, **95**, 47 (1949).

[16] Available from the Fluorochemical Dept., Minnesota Mining and Manufacturing Co., St. Paul 6, Minnesota.

TABLE I

CONSOLUTE TEMPERATURES, $t$°C., OF SOLUTIONS OF $(C_4F_9)_3N$ AT VARIOUS VOLUME FRACTIONS, $\phi_2$, AND MOLE FRACTIONS, $x_2$, OF $(C_4F_9)_3N$

| Methylcyclohexane | | | $n$-hexane | | | Isoöctane | | |
|---|---|---|---|---|---|---|---|---|
| $\phi_2$ | $x_2$ | $t$ | $\phi_2$ | $x_2$ | $t$ | $\phi_2$ | $x_2$ | $t$ |
| 0.00998 | 0.00357 | 19.2 | 0.0480 | 0.0181 | 25.5 | 0.0480 | 0.0228 | 16.7 |
| .0196 | .00714 | 36.0 | .0917 | .0369 | 40.4 | .0916 | .0445 | 31.4 |
| .0570 | .0214 | 66.3 | .168 | .0688 | 54.6 | .168 | .0853 | 46.0 |
| .0915 | .0348 | 79.4 | .287 | .129 | 59.6 | .287 | .1571 | 52.3 |
| .155 | .0672 | 92.6 | .377 | .182 | 60.5 | .359 | .206 | 53.8 |
| .267 | .126 | 97.5 | .447 | .228 | 60.4 | .377 | .219 | 53.6 |
| .354 | .216 | 98.3 | .502 | .270 | 60.1 | .418 | .250 | 53.5 |
| .412 | .224 | 97.6 | .558 | .316 | 59.0 | .456 | .280 | 53.1 |
| .501 | .265 | 96.7 | .627 | .381 | 57.1 | .502 | .318 | 52.4 |
| .556 | .310 | 95.7 | .716 | .480 | 51.3 | .558 | .368 | 51.8 |
| .627 | .375 | 92.9 | .834 | .649 | 34.8 | .627 | .437 | 50.4 |
| .716 | .474 | 85.5 | .910 | .787 | 14.2 | .716 | .538 | 44.9 |
| .834 | .643 | 63.4 | | | | .834 | .700 | 28.0 |
| .910 | .783 | 37.7 | | | | .871 | .757 | 20.4 |
| .951 | .878 | 8.9 | | | | .903 | .824 | <10 |

$vs.$ $\phi_2$, the volume fraction of $(C_4F_9)_3N$; the data for the curves are summarized in Table I. We further measured the vapor pressure of $(C_4F_9)_3N$ at two temperatures: 25.05°, 0.552 ± 0.001 mm.; 45.00°, 2.371 ± 0.015 mm. The heat of vaporization for this compound at 25° was calculated as 13,250 cal./mole.

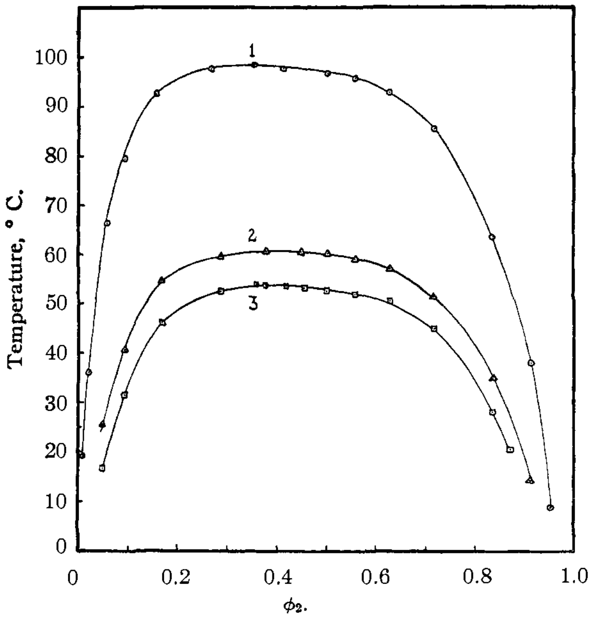

Fig. 1.—Critical solution temperature curves of $(C_4F_9)_3N$ with: 1, methylcyclohexane; 2, $n$-hexane; 3, isoöctane ($\phi_2$ = volume fraction of $(C_4F_9)_3N$).

## Comparison with Theory

The two fundamental equations in the field of solutions of non-electrolytes are

$$\ln\left(\frac{a_2}{x_2}\right) = v_2\phi_1^2(\delta_1 - \delta_2)^2/RT \qquad (1)$$

$$\ln\left(\frac{a_2}{\phi_2}\right) = \phi_1\left(1 - \frac{v_2}{v_1}\right) + v_2\phi_1^2(\delta_1 - \delta_2)^2/RT \quad (2)$$

where the subscript 1 refers to component 1 (the hydrocarbon in our case), subscript 2 refers to component 2 (the fluorocarbon), the $a$'s the activities, the $x$ the mole fraction, the $\phi$'s the volume fractions, and the $v$'s the molar volumes. The $\delta$'s, the solubility parameters, represent the square root of the energy of vaporization per ml. of the pure substances. Equation 1 applies to "regular" solutions, the components of which have approximately the same molar volumes; equation 2 is used for those cases where the components have significantly different molar volumes, as in our present case. Hildebrand has derived[6] the following equations from the above.

$$4RT_c \cong (v_1 + v_2)(\delta_2 - \delta_1)^2 \qquad (3)$$

$$\phi_{2,c} = \frac{v_1^{1/2}}{v_1^{1/2} + v_2^{1/2}} \qquad (4)$$

$$RT_c = \frac{2v_1v_2}{(v_1^{1/2} + v_2^{1/2})^2}(\delta_2 - \delta_1)^2 \qquad (5)$$

The first of these is derived from eq. 1, while the latter two are derived from eq. 2. Here the molar volumes and solubility parameters refer to values at $T_c$. Although these equations are approximate, nevertheless they have been used[1] satisfactorily to demonstrate agreement or disagreement with theory.

We wish first to compare the observed and calculated $\phi_{2,c}$; the calculations will be approximate since we do not have the values for the molar volumes at $T_c$. If, in the case of $n$-hexane, we take $v_1$ as 139 (from $d$ = 0.622 g./ml. at 60°), and $v_2$ as 376 (assuming a 5% increase in $v$ from 25 to 60°, similar to $n$-perfluoroheptane[6]), then eq. 4 yields a value of 0.378. If one instead uses this equation with $v_1$ = 131.7 and $v_2$ = 358.4, the values at 25°, one obtains an identical answer for $\phi_{2,c}$. The experimentally observed value is 0.40. The comparisons for the other pairs are given in Table II. Since the error in reading $\phi_{2,c}$ from the curves is ±0.02 due to the flatness at their tops we conclude that on the basis of this approximate method of comparison that eq. 4 and the theory *do* predict $\phi_{2,c}$ satisfactorily.

An approximate comparison between the observed $T_c$ and those calculated by means of eqs. 3 and 5 is also given in Table II. Molar volumes at 25° were used for all of the calculated columns. It is seen that none of the calculations based on the theory gives agreement and of these only in column

TABLE II

COMPARISON WITH THEORY

Subscript 1 = hydrocarbon; subscript 2 = $(C_4F_9)_3N$

| Solvent | $\phi_{2,c}$ |  | $T_c$ |  |  |  |  | $(\delta_1 - \delta_2)$ and $\delta_2$ at 25° Calcd. from: |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  | Calcd. Eq. 3 $(\delta_1 - \delta_2)$ from: |  | Calcd. Eq. 5 $(\delta_1 - \delta_2)$ from: |  | Eq. 6 |  | Eq. 3 |  | Eq. 5 |  | Eq. 7 |  |
|  | Obsd. | Calcd. Eq. 4 | Obsd. | Eq. 7 | Eq. 6 | Eq. 7 | Eq. 6 | $(\delta_1 - \delta_2)$ | $\delta_2$ | $(\delta_1 - \delta_2)$ | $\delta_2$ | $(\delta_1 - \delta_2)$ | $\delta_2$ | $(\delta_1 - \delta_2)$ | $\delta_2$ |
| Methylcyclohexane | 0.35 | 0.37 | 371.6 | 652 | 245 | 538 | 202 | 2.0 | 5.9 | 2.46 | 5.39 | 2.70 | 5.15 | 3.28 | 4.57 |
| *n*-Hexane | .40 | .38 | 333.8 | 544 | 121 | 394 | 86 | 1.4 | 5.9 | 2.33 | 4.97 | 2.55 | 4.75 | 3.00 | 4.30 |
| Isoöctane | .38 | .40 | 326.9 | 448 | 169 | 407 | 153 | 1.6 | 5.9 | 2.22 | 5.23 | 2.34 | 5.11 | 2.61 | 4.84 |

TABLE III

DATA FOR SOLUTIONS OF $(C_4F_9)_3N$ (2) IN VARIOUS SOLVENTS (1) AT 25°

$v_2$ = 358.4 ml./mole

| Solvent | $v_1$ | $\delta_1$ | $\phi_{1A}$ | $\phi_{1B}$ | $\phi_{2A}$ | $\phi_{2B}$ | Eq. 3 $(\delta_1 - \delta_2)$ | $\delta_2$ |
|---|---|---|---|---|---|---|---|---|
| Methylcyclohexane | 128.3[a] | 7.85[b] | 0.987 | 0.066 | 0.0129 | 0.934 | 3.28 | 4.57 |
| *n*-Hexane | 131.7[a] | 7.30[b] | .954 | .126 | .0460 | .874 | 3.00 | 4.30 |
| Isoöctane | 166.0[a] | 7.45[c] | .928 | .151 | .0719 | .849 | 2.61 | 4.84 |
|  |  |  |  |  |  |  |  | Av. = 4.57 |

[a] Calculated from mol. wt. and $d_{25}$ found in ref. 19. [b] Ref. 7. [c] Ref. 18.

2 (under $T_c$) do we have even the proper descending sequence of values. Admittedly this comparison is very rough, but it serves to indicate the anomalous behavior of our fluorocarbon–hydrocarbons liquid pairs. This method has been used previously[5] to show a general agreement with solubility theory for the cases of perfluoromethylcyclohexane in $CCl_4$, in $CHCl_3$ and in benzene.

A final and significant method of pointing out the anomalous behavior of our liquid pairs is to compare $(\delta_1 - \delta_2)$, obtained essentially from heats of vaporization, with $(\delta_1 - \delta_2)$ calculated from various equations developed from the theory. The value of $\delta_2$ of 5.9 for $(C_4F_9)_3N$ was calculated from the following equation using $\Delta H_{29} = 13{,}250$ cal./mole obtained from the vapor pressure data. The

$$\delta = \left(\frac{\Delta H^v_{298} - RT}{v}\right)^{1/2} \quad (6)$$

$(\delta_1 - \delta_2)$ values in the first column in this section in Table II were obtained with the $\delta_1$ values listed in Table III. The use of eqs. 3 and 5, using the observed $T_c$, and the values of the $v$'s at 25°, leads to the values shown. There is agreement between the results of these two equations, but each is in disagreement with the results obtained from eq. 6, based on vapor pressure measurements. Equations 3 and 5 lead to a $\delta_2$ value for $(C_4F_9)_3N$ of 5.0 to 5.2, while eq. 6 yields a value of 5.9.

Since in eqs. 3 and 5 we did not use the molar volumes and solubility parameter values for the constituents at the critical temperatures, we used another equation which avoided this complication. This equation can be derived[17] as follows: since the fluoramine is partially soluble in a given solvent and the latter in it to some degree at one temperature (25°), then at equilibrium the activity of the fluoramine in the one phase (low $\phi_2$ value) is equal to its activity in the other phase (at high $\phi_2$ value). Equation 2 is assumed to hold in both phases. Simplification results in the final eq. 7

$$\frac{1}{2}RT\left[\frac{1}{v_1}\ln\frac{\phi_{1A}}{\phi_{1B}} + \frac{1}{v_2}\ln\frac{\phi_{2B}}{\phi_{2A}}\right] + (\phi_{2A} - \phi_{2B})(\delta_1 - \delta_2)^2 = 0 \quad (7)$$

Here the subscript 1 refers to the usual organic solvent, the hydrocarbons in our case; subscript 2 to the fluoramine; subscript A to phase A (low $\phi_2$); and subscript B to phase B (high $\phi_2$). The necessary constants, data and results are summarized in Table III and the final $(\delta_1 - \delta_2)$ values and $\delta_2$-value for $(C_4F_9)_3N$ again given in Table II. The $\phi$ values in Table III are obtained from the intersection of the 25° isotherm with the curves in Fig. 1. A comparison of the $(\delta_1 - \delta_2)$ values obtained from this equation with those from eq. 6 reveals still greater discrepancies. Further the average $\delta_2$ value of 4.6 is the lowest $\delta_2$ value yet calculated and exhibits the greatest deviation from the value of 5.9 obtained from the heats of vaporization.

The solubility parameter of 5.9 for $(C_4F_9)_3N$ agrees well with the value of 5.7 obtained by McLaughlin and Scott[14] from the solubility of iodine and stannic iodide. Our experimentally determined result of 4.6 compares very favorably with the value of 4.7–4.8 obtained by these same two investigators from the solubility of phenanthrene in the same fluorocarbon. The behavior of $(C_4F_9)_3N$ is then in accord with previously observed anomalous behavior, *i.e.*, the fluorocarbon behaves normally with the standard solutes and the solubility can be explained satisfactorily in terms of regular solution theory, but behaves abnormally with hydrocarbons and the latter systems are not completely in accord with the theory. The hydrocarbons used in this work are evidently poorer solvents for the fluorocarbon than might be deduced from their heats of vaporization. This agrees with previous observations[6,18] on hydrocarbons. It must be concluded that the hydrocarbons are in themselves mainly responsible for the anomalous behavior.

This behavior is explained equally well by either the proposal of Hildebrand[18] or the "interpenetration theory" of Simons and Dunlap[9]; these interpretations are actually mutually exclusive. Hildebrand's suggestion implies that the hydrocarbons possess increased solvent power for substances of higher solubility parameter; he suggested that the

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[17] Derived in the main by Prof. J. H. Hildebrand (private communication) and completed by us.

[18] J. H. Hildebrand, *J. Chem Phys.*, **18**, 1337 (1950).

solubility parameters of the hydrocarbons be empirically increased by 0.6 of a parameter unit over the value calculated from their heats of vaporization. If this be done in our present work, then the solubility parameter of $(C_4F_9)_3N$ is raised from 4.6 to about 5.2 which is closer to its value of 5.7 as obtained by McLaughlin and Scott. It appears from this work that the solubility parameter values for our hydrocarbons should be enhanced by about 1.1–1.3 solubility parameter unit in order to obtain agreement with the solubility value of 5.7 and the heat of vaporization value of 5.9.

As an interesting conclusion, we might compare our fluorocarbon with other members of the series. If we plot the vapor pressures for the other members of the homologous series (3M Co. data) as shown in Fig. 2, we obtain the heats of vaporization at 25° and the solubility parameters (calculated by means of equation 6) shown in Table IV. We have included in this table other pertinent information supplied mainly by the 3M Co. There is no reason to expect any significant differences in the solubility parameters and indeed each has a value of 5.9–6.0 when calculated from its heat of vaporization. The original 3M Co. data for $(C_4F_9)_3N$ yielded a solubility parameter value of 6.9 which was out of line with the other values; this discrepancy led us to a redetermination of its vapor pressure.

TABLE IV

| | $(C_2F_5)_3N$ | $(C_2F_5)_2$ $(C_3F_7)N$ | $(C_3F_7)_3N$ | $(C_4F_9)_3N$ |
|---|---|---|---|---|
| Mol. wt. | 371 | 421 | 507 | 671 |
| $d_{20}$ | 1.749 | 1.765 | 1.832 | 1.883 |
| $d_{25}$ | 1.734 | 1.752[b] | 1.820 | 1.872 |
| $v_{20}$, ml./mole | 212.1 | 238.5 | 276.4 | 356.4 |
| $v_{25}$, ml./mole | 214.0 | 240.3 | 278.6 | 358.4 |
| B.p., °C. | 69.3°[a] | 91.2°[b] | 129.4°[c] | 177°[d] |
| $\Delta H^V_{298}$ | 8356 | 8900 | 10,280 | 17,170(3M Co.)<br>13,250(ours) |
| $\delta$, (eq. 6) | 6.0 | 5.9 | 5.9 | 6.9(3M Co.)<br>5.9(ours) |

[a] R. N. Haszeldine and A. G. Sharpe, "Fluorine and Its Compounds," John Wiley and Sons, New York, N. Y., 1951, p. 145, report a b.p. of 70°. [b] T. J. Brice and R. I. Coon, THIS JOURNAL, **75**, 2921 (1953), of the 3M Co., report the following measured data for this compound: $d_{25}$ 1.7537, b.p. 90.5°, $n^{25}D$ 1.2688. [c] Ref. *a* reports a b.p. of 130°. [d] Ref. *a* reports a b.p. of 179°.

## Experimental

**Critical Solution Temperatures.**—The $(C_4F_9)_3N$ sample (1030 g.) was distilled slowly over a ten-hour period through an all-glass, small helical-packed, 70 cm.-long Podbielniak column; the middle fraction boiling at 172.0–174.0° (at 741.5 mm.) was used for subsequent work. Its average density (25°) was 1.8839 as compared to the 3M Co. value of 1.872. Its reported refractive index, $n^{25}D$, of 1.2910 is below the Abbe limit of 1.30 so this property could not be checked.

Spectral grade (Phillips 66) isoöctane (2,2,4-trimethylpentane) was used without further purification. Its refractive index, $n^{25}D$, measured on the thermostated Abbe refractrometer was 1.3883. The literature value[19] is 1.38906.

High purity *n*-hexane (Phillips 66, 99 mole % min.) was used also without further purification. Its refractive index was found to be $n^{25}D$ 1.3749; the literature value[19] is 1.3723.

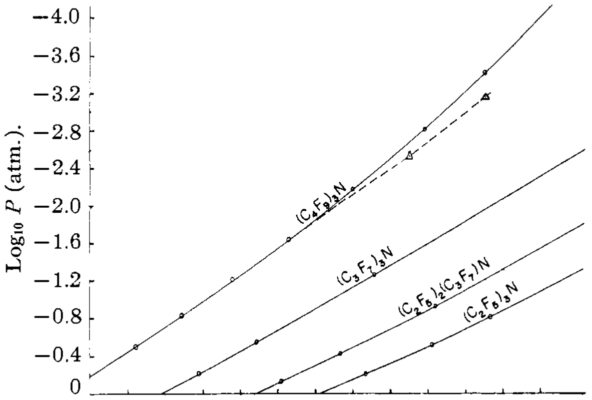

Fig. 2.—Vapor pressure plot for the fluoramines: ⊙, Minnesota Mining Co. data; △, our data.

The sample of methylcyclohexane (Matheson, practical) was distilled slowly through a Vigreux column and the middle fraction boiling at 99.0–99.6° (cor.) at 741.1 mm. was used. The boiling point is given in the literature[19] as 100.8–100.9°. Its refractive index $n^{25}D$ was measured on the Abbe to be 1.4223; the literature value[19] for this refractive index is 1.4206.

The temperature was measured with a 0–100° thermometer on which the smallest divisions were 0.1°. This thermometer was initially calibrated against a Bureau of Standards 0–100° thermometer.

The critical solution temperatures of the liquid–liquid mixtures were obtained as follows: pipetted quantities of the solvent (methylcyclohexane, *n*-hexane or isoöctane) were added to a pipetted amount of the $(C_4F_9)_3N$ in a test-tube which was contained inside of another larger test-tube. The whole was heated either in air or in water above the critical solution point and allowed to cool; the air space between the tubes permitted a slow cooling to take place. The temperature at which opalescence was first noticed with continual stirring was recorded as the consolute solution temperature for that composition. Each point was determined at least three times.

**Vapor Pressure of $(C_4F_9)_3N$.**—The apparatus was set up as shown in Bent's paper[20]; Redemann's modification of the saturator[21] was used.

This method is a dynamic one in which a known volume of dry gas, $N_2$, is passed slowly through a purified sample of the fluoramine and the saturated gas passed through a cold trap spiral. The gain in weight of the spiral, plus the temperature and atmospheric pressure on the gas initially plus its molecular weight enable one to calculate the vapor pressure of the amine.

The apparatus and technique was first checked by determining the vapor pressure of conductivity water at 25.05°. A 4-liter bottle of nitrogen gas was used; the gas was displaced into the system by allowing distilled water to siphon at a constant suitable rate (using a modified Redemann-type regulator) into the bottle. A convenient total time for a run is of the order of 3–4 hours. Liquid nitrogen traps were used. Two runs were made with water at 25.05°; the measured vapor pressure was 23.82 ± 0.01 mm. The International Critical Tables, Vol. III, p. 212, yields an interpolated value of 23.82 mm. The temperature variation (Beckmann) was ±0.006°.

Two runs were made with the fluoramine at 25.05°; a 19-liter source bottle of nitrogen gas was used. A second condensing glass spiral was used here also (as in the case of water) to catch any traces of the amine vapor not condensed in the first trap. The vapor pressure of the fluoramine at 25.05° was found to be 0.552 ± 0.001 mm. This value is substantially higher than the 3M Co. reported value of 0.3 mm. The temperature variation here was ±0.005°. Two runs were also made at 45.0° and the result of the vapor pressure determinations was 2.371 ± 0.015 mm.

**Acknowledgment.**—We are indebted to Dr. L. J. Hals of the Fluorochemical Department of Minnesota Mining and Manufacturing Co., for the sample

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[19] J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publ. Co., Inc., New York, N. Y., 1950.

[20] H. E. Bent and R. J. Francel, THIS JOURNAL, **70**, 634 (1948).

[21] C. E. Redemann, *et al.*, *ibid.*, **70**, 631 (1948).

of $(C_4F_9)_3N$ used as well as for the data supplied. We also wish to thank Professor Joel H. Hildebrand for constructive criticisms of this paper

CHICAGO, ILLINOIS

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA]

# Physical and Thermodynamic Properties of Terpenes.[1] III. The Vapor Pressures of α-Pinene and β-Pinene[2]

BY J. ERSKINE HAWKINS AND GEORGE T. ARMSTRONG

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The vapor pressure-temperature relations for α-pinene and for β-pinene between 15° and their normal boiling points are recorded. Equations to express these relations are presented. The data indicate the normal boiling points to be 155.9 ± 0.1° for α-pinene and 166.0 ± 0.1° for β-pinene.

A survey of the literature discloses considerable uncertainty in the vapor pressure-temperature relations of α-pinene and β-pinene. In some cases compounds used for the determinations were of doubtful purity, and in other cases the data cover only relatively short ranges of temperature and pressure.

Pickett and Peterson[3] used α-pinene, of which 5% boiled below 155° and 95% below 158°. They measured the vapor pressures from 4 to 623 mm. The same workers made similar measurements between 3 and 381 mm. with β-pinene of which 5% boiled below 160.2° and 95% below 163.8°. They measured the pressures to 0.1 mm. below 432 mm. and apparently to only 1.0 mm. at the higher pressures. The temperatures were measured to 0.1° over the whole range. E. G. Linder[4] measured the vapor pressures of α-pinene at three temperatures between −6 and 13.25°. The α-pinene used in this case was of unstated purity. Rudakov and Korotov[5] twice distilled crude turpentine, *Pinus sylvestrus*, through a two-meter du Pont column and obtained α-pinene for which they claimed a high degree of purity. They measured the vapor pressures of the pinene between 49 and 200 mm. and determined the boiling point at atmospheric pressure. Fuguitt, Stallcup and Hawkins[6] determined the boiling points of α-pinene and β-pinene at pressures from 15 to 76 mm. Both compounds were fractionated to a high degree of purity.

The uncertainty in the normal boiling points is indicated by the wide range of temperatures reported.[7] In the case of α-pinene these temperatures range from 154.5–155°, as determined by Nametkin,[8] to 158.5–159°, as found by Perkin.[9] For β-pinene the normal boiling point ranges from 156–157°, as determined by Slawinski, Piliczewski and Zacharewicz,[10] to 164–166°, as reported by Schorger[11] and Wallach.[12]

In view of the existing situation, the determination of the temperature-vapor pressure relations over a wide range for α-pinene and β-pinene of a high degree of purity was undertaken. The method used was essentially that devised by Ramsay and Young[13] and modified by Ryan and Lantz.[14]

## Preparation of Materials

**α-Pinene and β-Pinene.**—These materials were prepared from the commercial products by the procedure previously described.[6] The constants of α-pinene were: $n^{25}_D$ 1.4631–1.4632, $d^{25}_4$ 0.8539, $[\alpha]^{25}_D$ +29.12. The constants of β-pinene were : $n^{25}_D$ 1.4768, $d^{25}_4$ 0.8667, $[\alpha]^{25}_D$ −18.54. Recent cryoscopic measurements on pinenes having these physical constants indicate a purity of approximately 99.6 and 98.7 mole %, respectively. It is believed that the impurities are of a nature that would not significantly affect the vapor pressures.

**Other Materials.**—The substances used for the calibration of the thermo-element were recrystallized sodium sulfate decahydrate, a National Bureau of Standards sample of tin, and highly purified water which contained about 2.3 parts per million of dissolved solids. This amount of solids would not affect the ice point as much as 0.001°.

A series of commercial grade liquids whose boiling points ranged from 46 to 170° was used to provide a constant temperature vapor-bath at the various pressures at which measurements were made.

## Apparatus

In general, the apparatus was of conventional design.

**Pressure Regulation and Measurement.**—A constant pressure was maintained by use of a manostat of the type designed by Hershberg and Huntress.[15] The pressure fluctuation was reduced by the 18-liter reservoir placed in series between the pump and manostat and the boiler and the manometer. Below 400 mm. the pressure variations were not observable and at higher pressures were within 0.1 mm. The manometer was constructed and operated according to the directions of Germann.[16] The mercury levels were determined by a cathetometer reading to 0.01 mm. The adjustment of the cross-hair on the meniscus of the mercury was simplified by placing a piece of black paper a few millimeters above and behind the surface of the mercury. The pressures were corrected to correspond to the density of mercury at 0° and the value of gravity at 45° latitude and sea level on the basis that Gainesville is at

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(1) For the first article in this series see footnote 6, and for the second see THIS JOURNAL, **76**, 2669 (1954).

(2) The material included in this publication is based upon a thesis presented by George T. Armstrong to the Graduate Council of the University of Florida in partial fulfillment of the requirements for the degree of Master of Science, February, 1943.

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