ISSN: 0101-3742

SOME PHYSICAL AND THERMODYNAMIC PROPERTIES OF n–C_nF_{2n+2} COMPOUNDS WITH n = 4 – 8

M. CAMPOS-VALLETTE*
G. DIAZ F.**

ABSTRACT

Thermodynamic constants (C_v, C_p and π_i) and physical properties (β_T, α, β_S and v) of the n–C_nF_{2n+2} compounds with n=4 to 8 were evaluted and estimated from correlations. The values are compared with those obtained for the corresponding molecules in the n–C_nH_{2n+2} series and the results were found to be consistent with the published experimental data. The liquid structure or n–perfluorated compounds is discussed on the basis of these data.

INTRODUCTION

Physical and thermodynamic properties of n–alkanes have been a topic of extensive studies for a long time and are well documented in the literature. However, few works have dealt with the corresponding n–perfluoro compounds and the existing data is scattered in different sources /1-4/.

In this work, physical and thermodynamic constants for the n–C_nF_{2n+2} series, with n = 4 to 8, are reported and a comparison with the values for the corresponding n–paraffins is attempted.

Values for the heat capacity at constant volume and pressure C_v and C_p, the internal pressure π_i, the isothermal compressibility, β_T, the expansion coefficient, α, the adiabatic compressibility, β_s, and the velocity of sound, v are proposed.

Correlations from the obtained experimental data in conjuction with the statistical model of liquids recently developed by Chandler et al. /5/ are used to gain some insight on the liquid structure of the n–perfluorated compounds.

CALCULATIONS

The π_i value can be determined experimentally from the relationship $(\partial P/\partial T)_V$/6/ or calculated from α and β_T through eq. 1.

$$\pi_i + p = \left(\frac{\alpha}{\beta_T}\right) T \qquad (1)$$

where $\alpha = (1/V)\,(\partial V/\partial T)_p$ and $\beta_t = -(1/V)\,(\partial V/\partial P)T$. Under standart conditions P is far lower than π_i, therefore, in such conditions may be neglected. Since the thermal compressibility coefficients are not ayailable they be obtained from.

$$\beta_T/\beta_s = C_p/C_v \qquad (2)$$

with $$C_p/C_v = (\alpha^2 TMv^2/C_p) + 1 \qquad (3)$$

and $$\beta_s = 1/v^2 d \qquad (4)$$

where M is the molecular weight and d the density.

RESULTS

The expansion coefficients for the n–perfluoroalkanes in C_4 to C_7 were calculated by differentiating the density respect to the temperature. (2, 7 – 12).

The graph of α versus the number of carbon atoms for the n–perfluoroalkanes shows the same type of curve than that observed for the corresponding n–alkanes[13] (Fig. 1); the α value for n–C_8F_{18} may then be obtained by extrapolation.

Some measurements of the velocity of sound have been published for n–C_5F_{12} and n–C_6F_{14} below 273 K[9] and for n–C_7F_{16} between 293 K and 333 K[14]. Considering that v for most non-associated liquids is a linear function of the temperature[14] it is possible to calculate v at 298 K. The velocity of sound for n–C_8F_{18} and n–C_4F_{10} have been obtained by extraplating the curve obtained by plotting v versus molecular weight at room temperature (Fig. 2).

The adiabatic compressibility for n–perfluoroalkanes and the corresponding n–paraffins was calculated at 298 K through eq. 4. With these values and those reported β_T (6,15) β_T/β_s ratio of 1.3 for the n–alkanes from C_5 to C_8 was obtained. This ratio was used to calculate β_T for n–C_4H_{10} which had not been published yet.

The above results for the n–perfluoroalkanes and their corresponding n–paraffins at 298 K are collected in Table I.

The β_s values proposed in this work have also been considered to calculate β_T for C_4 and C_8 n–perfluorated compounds (not published at present), through the ratio C_p/C_v (Eq. 2).

The experimental heat capacities at constant pressure for the C_6 and C_8 n–perfluorated molecules[17] and for the C_5 to C_8 n–alkanes[18] are shown in Table II. The C_p values for n–C_5F_{12} and n–C_7F_{16} were interpolated (Fig. 3); the C_p data for n–C_4F_{10} has been calculated by SARGENT et alii[19]. The C_p value for n–C_4H_{10} was obtained by extrapolating the curve corresponding to n–alkanes (Fig. 3).

An approximate C_p/C_v ratio of 1.32 at 293 K was obtained for the n–C_nF

* Departamento de Química Universidad de Chile Casilla 653 – Santiago CHILE.
** Academia Superior de Ciencias Pedagógicas Casilla 34-V Valparaíso CHILE.

C_{2n+2} (with n = 4 to 8) series by inserting in eq. 3 the values of C_p, α and v proposed in this work. The isothermal compressibility, β_T, was then obtained through eq. 2 as a function of the β_s values reported above. The β_T data are shown in Table I and compared with the data available.

Internal pressure data has been reported for n–C_5F_{12}[10], n–C_6F_{14}[21] and n–C_7F_{16}[22]; for the n–C_4F_{10} there is only one determination at 260 K[7]. No value has been published for n–C_8F_{18}. The π_i values at 298 K for the n-perfluoroalkanes were calculated with α and β_T data proposed in the present work. For the n–paraffins in C_5, C_7 and C_8, the internal pressure was determined from measurements of volume at differnt pressures and temperatures taken from the literature[6]. The evaluated constants are shown in Table III and compared with reported data.

DISCUSSION

A. Physical constants.

The similatity between plots of α versus the number of carbon atoms for the n–perfluorated and n–alkanes compounds (Fig. 1) indicate that the best α values calculated for n–C_5F_{12} and n–C_6F_{14} are those found from density data in references 8, 9 and 2 respectively.

The compressibilities of the n–perfluorated liquids are found to be twice larger than those corresponding to n–alkanes, Table I. In both series of molecules β decreases proportionally as the number of carbon atoms increases

For the n–alkanes and the n–perfluorated compounds the absolute viscosity, η is about three time smaller than that corresponding to the n–perfluoroalkanes[3, 9, 14]. However, the viscosity of the n–perfluorate compounds is very sensitive to temperature and decreases as the temperature increases[3, 13].

The velocity of sound in liquids is proportional to σ^{-9} where σ is the mean distance between particles at a given temperature[16]. The observed v values for the n–alkanes are approximatively twice larger than the n–perfluoroalkanes (Table I). A low sound velocity derives from a weak intermolecular interaction potential, a characteristic feature of perfluorocarbons.

The observed correlations of the different parameters studied here for both series of molecules agree well with reported data[9, 21, 22].

From the above results, the calculated constants for the n–perfluoroalkanes are consistent with the existence of numerous large-size cavities in the liquid state. A similar conclusion has been obtained from NMR studies in analogous systems[24]. The existence of the cavities may explain the ability of these compounds for dissolving gases. On the other hand, the F....F intermolecular repulsion must make the interactions between the n–perfluorated molecules weaker than those existing in n–alkanes and this behaviour is clearly seen from the calculated pysical constants.

The above conclusions agree with Chandler's view that the structure of non associated nonpolar liquids mainly depends on the shpae of their molecules[4].

B. Thermodynamical constants.

The hight value for the C_p/C_v ratio of n–C_4F_{10} is probably due to the uncertatinty in velocity of sound obtained by extrapolation or by the calculated C_p value[19]. The publised heat capacity for n–C_7F_{16}[20] does not follow the tendency observed here. Fig. 2 and Table I.

The calculated internal pressures shown in Table III agree well with the reported experimental data. In general for normal liquids the π_i decreases as the temperature increases, so the n–C_4H_{10} π_i value obtained by extrapolation[7] is not consistent with the above results.

In particular it is interesting to compare π_i of this work with the ratio $(\Delta H_1 - \Delta H_g)\Delta V_1$ deduced[25] from Chandler's theoretical considerations.

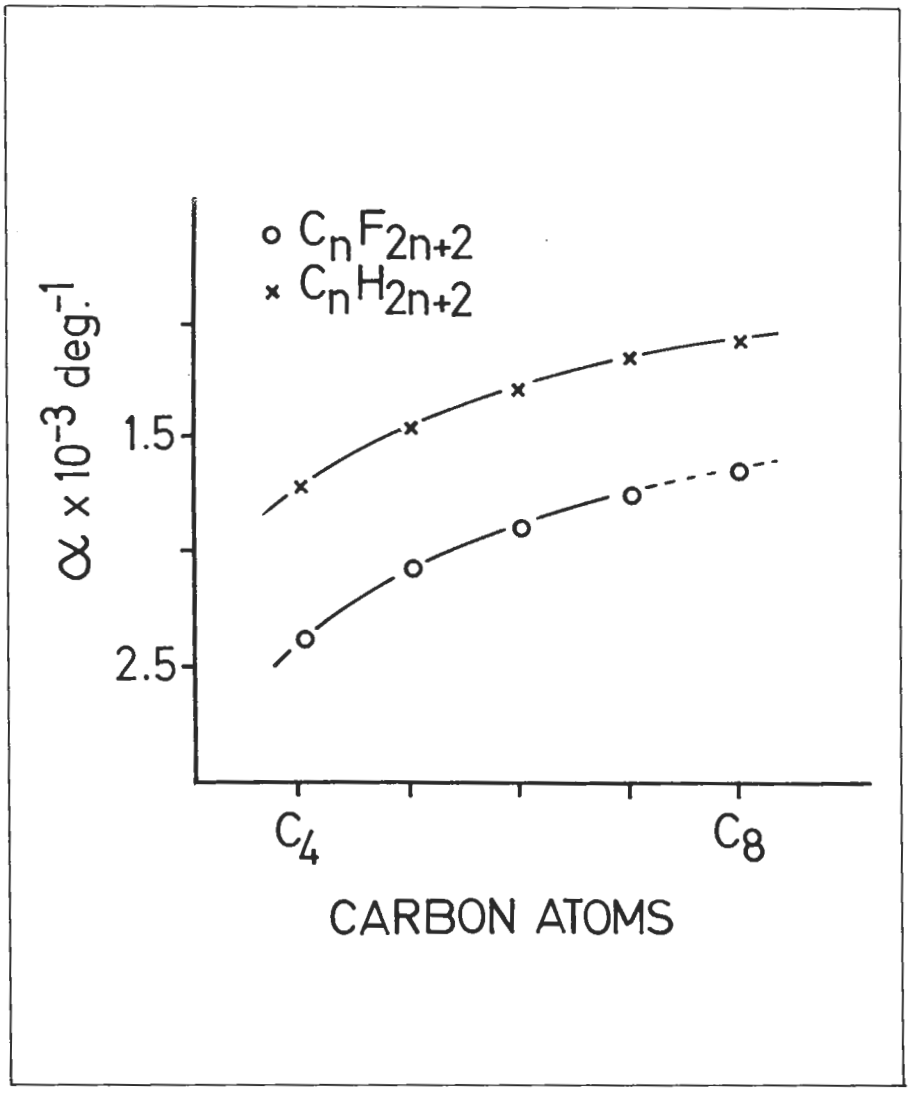

FIGURE 1
Expansion coefficient vs. number of carbon atoms at 298 K. The point on the discontinuous line is the extrapolated value

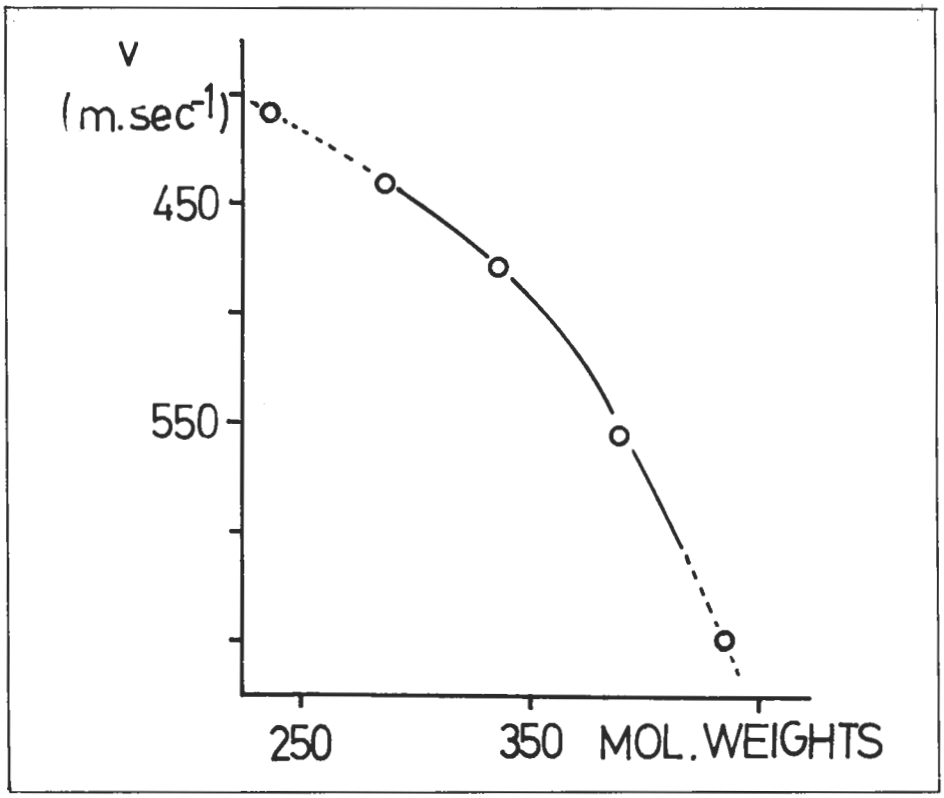

FIGURE 2
Velocity of sound, v, versus molecular weights for n–perfluoroalkanes at 298 K. The points on the discontinuous line are the extrapolated values.

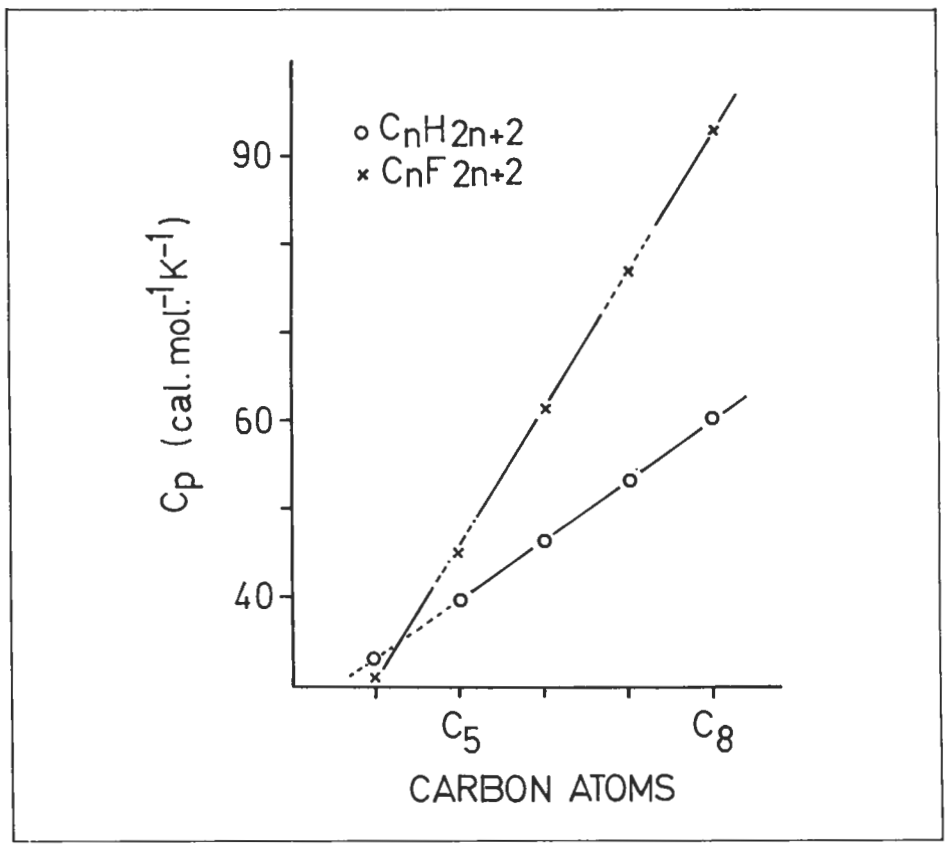

FIGURE 3
Heat capacity at constant pressure, C_p, vs. carbon atoms. The points on the discontinuous line are the interpolated or extrapolated values. X at 293 K and 0 at 290 K.

TABLE I. Some physical properties of n–perfluoralkanes and n–paraffins at 298 K.

	α[a]	v[b]	β_s[c]	β_T[c']	η[d]		α[f]	v	β_s	β_T	β_T/β_s	η[f]
n–C_4F_{10}	2.36/8/	410	4.10	5.42	1.17[e]	n–C_4H_{10}	1.71	964/14/	1.9	2.47	1.30	0.25
n–C_5F_{12}	2.06/9/	440	3.22	4.25 4.18/9/	1.27/9/	n–C_5H_{12}	1.45	1052/16/	1.47	1.8 1.8/6/	1.23 1.22	0.34
n–C_6F_{14}	1.88/2/	480	2.60	3.43 3.32/21/	1.51/9/	n–C_6H_{14}	1.30	1113/16/	1.24	1.61/15/	1.30	0.45
n–C_7F_{16}	1.75/12/	557	1.86	2.46 2.34/22/	2.0/3/	n–C_7H_{16}	1.21	1165/16/	1.09	1.42/15/	1.31	0.69
n–C_8F_{18}	1.6[e]	650	1.34	1.77	3.0[e]	n–C_8H_{18}	1.1	1238/16/	0.94	1.19/15/	1.27	0.98

a Thermal expansion coefficient ($\times 10^{-3}$ deg.$^{-1}$).
b Velocity of sound (m.sec^{-1}).
c,c' Adiabatic and isothermal compressibility coefficients ($\times 10^{-4}$ atm^{-1}).
d Viscosity (cp.) at 253 K.
e Extrapolated values.
f Reference /13/.

TABLE II. Heat capacity of n–perfluoroalkanes and n–paraffins.

	n–C_4F_{10}	n–C_5F_{12}	n–C_6F_{14}	n–C_7F_{16}	n–C_8F_{18}
C_p (liq)[a]	30.4 (293K)/19/	45.0 (293 K)	61 (293 K)/17/ 57.4 (273 K) 59.3 (273 K)/9/	94.3 (293 K)/20/ 77.0 (293 K)	93 (293 K)/17/
C_p/C_v (293 K)	1,5 /19/	1,4	1,3	1,3	1,3

	n–C_4H_{10}	n–C_5H_{12}	n–C_6H_{14}	n–C_7H_{16}	n–C_8H_{18}
c_p (liq)[b] (290K)	32.3[c]	39.34	46.07	53.04	59.98

a cal. mole^{-1}K^{-1}.
b 18
c extrapolated value

TABLE III. Internal pressure of n-perfluoroalkanes and n-paraffins.

	α/β_T[a]	π_i calc.[b]	π_i (ref)		α/β_T	π_i calc.	π_i (ref).
n–C_4F_{10}	7.73 (258 K) 4.50 (298 K)	2000(258 K) 1341 (298 K)	2274 (260 K)/7/	n–C_4H_{10}	6.92 (298 K)	2063 (298 K)	1880 (260K)/7/
n–C_5F_{12}	5.0 (298 K)	1490 (298 K)	1390 (300 K)/10/	n–C_5H_{12}	7.57 (293 K)	2220 (293 K)	2120 (300K)/10/ 2200 (298K)
n–C_6F_{14}	5.65 (298 K) 5.89 (303 K)/21/	1683 (298 K)	1784 (303 K)/21/	n–C_6H_{14}	8.12 (293 K) 8.0 (298 K)/21/	2379 (293 K)	2285 /23/ 2383 (298K)/21/
n–C_7F_{16}	7.35 (298 K) 7.46 (295 K)/22/ 6.97 (300 K)/22/	2190 (298 K)	2200 (293 K)/22/	n–C_7H_{16}	8.4 (293 K) 8.1 (293 K)	2461 (293 K) 2361 (293 K)	2580 (298K)
n–C_8F_{18}	9.3 (298 K)	2771 (298 K)		n–C_8H_{18}	8.72 (293 K)	2568 (293 K)	2452 (293 K)

a atm. deg.$^{-1}$.
b atm.

RESUMO

As propriedades físicas (β_T, α, β_S e v) e as constantes termodinâmicas (C_v, C_p e π_i) dos compostos $n-C_nF_{2n+2}$ com n= 4 até 8 foram avaliadas e estimadas a partir de correlações. Os valores são comparados com aqueles obtidos para as moléculas correspondentes nas séries $n-C_nF_{2n+2}$ e os resultados encontrados são consistentes com os dados experimentais da literatura. A estrutura líquida dos compostos n–perfluorados é discutida com base nesses dados.

REFERENCES

1. REED, T.M. *Fluorine Chemistry,* New York, Academic, 1964. v. 5.

2. GREEN, S.W. *Chem. Ind., 3:*63, 1969.

3. HUDLICKY, M. *Chem. of Organic Fluorine Compounds.* Pergamon Press, 1961. cap. 8.

4. CAMPOS-VALLETTE, M. Docteur ès Sciences. Thèse Univer. de Bordeaux I. Bordeaux, France, 1982.

5. CHANDLER, D. *Annu. Rev. Phys. Chem. 29:*441, 1978; C.S.HSU, L.R. PRATT and D. CHANDLER *J. Chem. Phys., 68:*4213, 1978; ibid *68:* 4202, 1978 and D. CHANDLER *J. Chem. Phys., 68:* 2959, 1978.

6. BRIDGMAN, P.W. *Proc. Am. Acad. Arts. Sci. 76:* 71, 1948.

7. SIMONS, J.H. &MAUSTELLER, J.W. *J. Chem. Phys., 20:* 1516, 1952.

8. BROWN, J.A. & MEARS, W.H. *J. Phys. Chem., 62:* 960, 1958.

9. COCHRAN, M.A.; NORTH, A.M.; PETHRICK, R.A. *J.Chem. Soc. Far Trans. 70:* 1274, 1974.

10. SIMONS, J.H. & DUNLAP, R.D. *J. Chem. Phys., 18:* 335, 1950.

11. DUNLAP, R.D.; MURPHY, J.C.; BEDFORD, R.C. *J. Am. Chem. Soc., 80:* 83, 1958.

12. FOWLER, O.; HAMILTON Jr., J.M.; KASPER, J.S.; WEBER, C.E.; BURFORD, W.B. ANDERSON, H.C. *Ind. Eng. Chem., 39:* 375, 1947.

13. SELECTED Values of Physical and Chemical Properties of Hydrocarbons. Am. Petrol. Inst. Res. Proy., Carnegie Press, 1951.

14. LAGEMANN, R.T.; WOOLF, W.E.; EVANS, J.S.; UNDERWOOD, N. *J. Am. Chem. Soc., 70:* 2994, 1948; LAGEMANN, R.T.; Mc MILLAN, Jr., D.R. WOOLSEY, M. *J. Chem. Phys., 16:* 247, 1948, LAGEMANN, R.T. & CORRY, J.E. ibid *10:* 759, 1942.

15. HANDBOOK of Chem. and Phys. 57 ed. CRS Press, 1976-1977.

16. RAMA RAO M. *J. Chem. Phys., 9:* 682, 1945.

17. CAMPOS-VALLETTE, M.; REY-LAFON, M.; LANGNIER R. *Chem. Phys. Lett. 89:* 189, 1982.

18. WITT, R.W. & KEMP, J.D. *J. Am. Chem. Soc. 59:* 273, 1937; LURIA M. &BERISON S.W. *J. Chem. Org. Data, 22:* 90, 1977.

19. SARGENT, J.W. & LAZERTE, J.D. *Amer. Soc. Test. Mater. Spect. Tech. Bull., 34b:* 51, 1964.

20. YARRINGTON, M. & KAY, W.B. *J. Phys. Chem., 61:* 1259, 1957.

21. DUNLAP, R.D. & SCOTT, R.F. *J. Phys Chem., 66:* 637, 1962.

22. SMITH, E.B. & HILDEBRAND, J.H. *J. Chem. Phys., 31:* 145, 1959.

23. GLASSTONE, S.; *Text book of Physical Chemistry.* 2 ed. D. Van Nostrand Co. Inc., 1946.

24. STEBE, M.J. Docteur -es Sciences These Université de Nacy I. Nacy, France 1980.

25. DEVAURE, J. & LASCOMBE, J. *Noveau J. de Chimie, 3:* 579, 1979.