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Evidence against Energetically Favored Coiling of Vapor-Phase Paraffins up to n-Tetracosane

Edwin F. Meyer* and Kenneth S. Stec

Contribution from the Department of Chemistry, De Paul University,
Chicago, Illinois 60614. Received December 10, 1970

Abstract: The evidence in the literature in favor of the coiling of vapor-phase paraffins into energetically favored, tight globular configurations has been reexamined. The dependence of energy and enthalpy of vaporization on the number of carbon atoms in a paraffin molecule is discussed, and it is shown that the latter is linear at constant temperature for molecules up to 24 carbons in length. It is concluded that no energetically favored vapor-phase coiling occurs in the molecules in question. The vapor pressure of zone-refined n-tetracosane has been measured between 225 and 292°; its Antoine equation is log p(cm Hg) = 6.31564 − 2289.02/(t + 125.23), with a standard deviation of 0.00015 in log p. Its surface tension has been measured between 60 and 150°, and follows the relation γ(dyne/cm) = −0.07476t + 30.9.

A method for estimating the contributions of the various types of cohesive energy to the total energy of attraction in polar organic liquids has recently been developed in this laboratory.[1,2] Its use of the energy of vaporization as a measure of the total energy of attraction in the liquid state has been questioned, since long-chain molecules allegedly give up a significant amount of energy during the vaporization process by coiling into compact globular configurations.[3] Thus the energy of vaporization would represent a quantity smaller than the total energy of attraction in the liquid by what we might call the "energy of coiling." We must emphasize that the coiling in question does not refer to the random deviations from the planar trans form of long chains, which certainly occur, but with which no significant energy lowering is associated. The term "coiling" in this paper refers to the process in which a randomly oriented vapor-phase molecule is converted to a compact globular configuration with the release of a quantity of energy.

Since the results in this laboratory indicate that no such coiling occurs, at least in paraffins up to 24 carbons in length, we have looked into the background of the coiling concept, and have found no sound experimental basis for it, at least in the range of our studies.

Langmuir[4] apparently provided the first ideas regarding coiling. He estimated the surface areas of coiled and uncoiled palmitic acid molecules and multiplied the difference by a surface energy typical of hydrocarbons to obtain the energy of coiling.[4b] Using the Boltzmann equation, he concluded that the uncoiled configuration would have to have an a priori probability more than a million times greater than that of the coiled one in order to be preferred in the vapor phase. Since this is very unlikely, the molecule would be expected to exist as a coiled-up "sphere."

(His calculations apply at a temperature of ~300°K. More will be said about this later in this paper.)

Aten[5] agreed with Langmuir's qualitative conclusions, and tested them against heats of vaporization for the paraffins. He had fundamentally sound ideas concerning the conditions under which the comparison should be made, but the data available at the time for long chains dated from 1882 and were incomplete. He was forced to make several approximations and his results cannot be considered conclusive.

Huggins[6] produced expressions for the total enthalpy of liquid and vapor hydrocarbons as functions of the number, n, of carbon atoms in the chain. This provided a theoretical basis for the dependence of the heat of vaporization of these molecules on n. His reasoning for the vapor phase followed Langmuir's and Aten's ideas, namely, that the extra enthalpy of the vapor when the long-chain molecule is coiled up into a sphere should be proportional to the exposed surface area, or $n^{2/3}$.

Wall, et al.,[7] measured energies of vaporization of some very long-chain paraffins, and tried correlating the heats of vaporization of paraffin molecules from C_4 to C_{24} with n. A linear dependence was found to be inadequate, while a plot of ΔH_{vap} vs. $n^{2/3}$ at constant temperature gave a satisfactory fit to the data. This result was taken as evidence for molecular coiling, in accord with the predictions of Langmuir[4] and Huggins.[6]

On the other hand, Meyer, et al.,[1,2] claim that the energy of vaporization at "corresponding" temperatures varies linearly with n to the first power. ("Corresponding" temperatures are those at which different members of the homologous series exhibit equal volumes per CH_2 group in the liquid phase.) These observations are not consistent; a resolution of the discrepancy is offered later in this paper.

(1) E. F. Meyer and R. E. Wagner, J. Phys. Chem., 70, 3162 (1966).
(2) E. F. Meyer, T. A. Renner, and K. S. Stec, ibid., 75, 642 (1971).
(3) M. L. Huggins, J. Paint Technol., 41, 509 (1969).
(4) (a) I. Langmuir, "Third Colloid Symposium Monograph," The Chemical Catalog Co., New York, N. Y., 1925, pp 53–54; (b) I. Langmuir in "Colloid Chemistry," Vol. I, J. Alexander, Ed., The Chemical Catalog Co., New York, N. Y., 1926, p 525.
(5) A. H. W. Aten, J. Chem. Phys., 5, 264 (1937).
(6) M. L. Huggins, J. Phys. Chem., 43, 1083 (1939).
(7) L. A. Wall, J. H. Flynn, and S. Straus, ibid., 74, 3237 (1970).

Experimental Section

The n-tetracosane was purchased from Humphrey Chemical Co. and purified in a Fisher Zone Refiner[8] (100 passes). Its vapor pressure was measured from 225 to 292° using an ebulliometer designed after Ambrose.[9] Pressures were measured using a manometer containing DC 704 oil, which was calibrated by measuring an identical pressure with a mercury manometer and the oil manometer. The manometers were thermostated to ±0.1°; pressures were corrected to centimeters mercury at 0° and standard gravity. Temperatures were measured with a platinum resistance thermometer traceable to the National Bureau of Standards, and a Leeds and Northrup G-2 Mueller Bridge.[10] Table I presents the experimental

Table I. Vapor Pressure of n-Tetracosane[a]

T, °C	p, cm Hg
225.66	0.6199
241.37	1.1795
252.23	1.7827
262.89	2.6172
277.57	4.2955
291.98	6.7485

[a] Log p (cm Hg) $= 6.31564 - 2289.02/(t + 125.23)$. Standard deviation in log p is 0.00015.

results, the Antoine equation obtained by least-squares analysis, and the standard deviation in log p. The surface tension of n-tetracosane was measured with a capillary rise technique in the range 60–150°. The rise was measured with a cathetometer capable of ±0.005-cm precision per reading, so the absolute error in the rise is 0.01 cm. Since the rise is in the order of 2–3 cm, the error is about 1%. The thermostat was controlled to 0.1°; temperatures were measured with a mercury in glass thermometer calibrated against an NBS platinum resistance thermometer. The results are presented in Table II.

Table II. Surface Tension of n-Tetracosane as a Function of Temperature[a]

T, °C	γ, dyn/cm
61.0	26.4
74.8	25.3
98.5	23.5
121.5	21.9
125.0	21.5
146.9	20.0
148.2	19.8

[a] The equation $\gamma = -0.07476t + 30.9$ reproduces these data with an average deviation of 0.05 dyn/cm.

Discussion

The energy of vaporization is readily calculated from the Antoine equation through the Clausius–Clapeyron equation and the relation, $\Delta H = \Delta E + RT$; thus

$$\Delta E_{vap} = RT\left[\frac{(2.303)(2289.02)T}{(t + 125.23)^2} - 1\right]$$

The "corresponding" temperature for n-tetracosane is that temperature at which its molar volume is 475.8 ml/mol; the empirical equations of Orwoll and Flory[11] yield a temperature of 156°. Calculation of an energy of vaporization at this temperature with data measured above 225° is questionable at best; however,

(8) Thanks are due Andy Sopcich for zone refining the n-tetracosane.
(9) D. Ambrose, J. Sci. Instrum., 41 (1968).
(10) We gratefully acknowledge a grant from the Research Corporation toward the purchase of the platinum resistance thermometer and resistance bridge.
(11) R. A. Orwoll and P. J. Flory, J. Amer. Chem. Soc., 89, 6814 (1967).

equivalent considerations at 200° (a far less drastic extrapolation) are presented later in this paper which support the ideas suggested by the initial calculation.

Using the data for the paraffins from C_5 through C_{12} it is found that each CH_2 group contributes 0.909 kcal/mol to the energy of vaporization from the "corresponding" state exhibiting 19.08 ml/mol of CH_2 groups. On this basis, n-tetracosane should display an energy of vaporization of 23.8 kcal/mol *if it does not coil into energetically favored "spheres."* The value calculated on the basis of our vapor pressures is 23.5 kcal/mol. Because of the extrapolation in temperature involved, this observation in itself is not conclusive evidence that no energetically favored coiling occurs; however, it led us to look further into the matter.

Antoine equations were collected[12] for the paraffins up to C_{20}, and included in a plot of energy of vaporization *vs.* n at "corresponding" temperatures. The results are shown in Figure 1. The straight line is very precise, producing energies within 0.1 kcal/mol of the measured values. The significance of this observation is that the line is based only on those paraffins containing 12 or less carbon atoms, most of which would not be expected to be able to display compact globular configurations. The implication is that each carbon atom in the chain contributes a fixed amount to the total interaction between molecules, and that an insignificant amount of energy is given up by a coiling process in the vapor phase.

(We may add parenthetically that our approach is fundamentally that of Aten.[5] He recognized that the comparison should be made with energies of vaporization at some kind of "reduced" temperature to take into account the closer approach of the longer chain molecules in the liquid phase. He expected that these energies of vaporization would be proportional to $n^{2/3}$, however, since he accepted the idea of vapor-phase coiling.)

It was stated above that a plot of energy of vaporization at "corresponding" temperatures cannot be linear with respect to n at the same time that a plot of enthalpy of vaporization at constant temperature is linear with respect to $n^{2/3}$. Consider the following thermodynamic cycle: starting with a given liquid paraffin at temperature T_i, (a) change its temperature to T_f, our "corresponding" temperature for that molecule; (b) vaporize 1 mol of the liquid; (c) change the temperature of the vapor back to T_i and its pressure to the vapor pressure at T_i; (d) condense 1 mol of the vapor. Since enthalpy is a state function, the total enthalpy change for the cycle is 0, and we can equate the negative of step d to the sum of the other three steps

$$-\Delta H_d = \Delta H_a + \Delta H_b + \Delta H_c$$

Assuming the enthalpy of the liquid is independent of pressure, we can write

$$\Delta H_a + \Delta H_c = \int_{T_i}^{T_f} [C_p^l - C_p^g]dT + \int_{P_i}^{P_i} \left(\frac{\partial H}{\partial P}\right)_T^g dP$$

In addition, we have

$$\Delta H_b = \Delta E_b + \Delta(PV)_b$$

(12) For the paraffins from C_9 to C_{15}, we used the data of D. L. Camin and F. D. Rossini, J. Phys. Chem., 59, 1173 (1955); for the remainder of the paraffins up to C_{20}, we used the API Project 44 Tables of 1953.
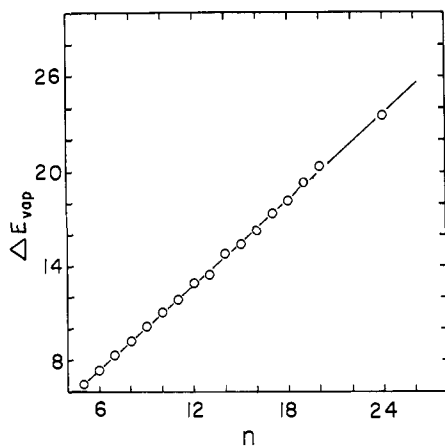
Figure 1. Energy of vaporization at "corresponding" temperatures (see text) as a function of the number of carbon atoms in the normal paraffins. The equation of the best line through the members up to C_{12} is $\Delta E = 2.00 + 0.9091n$.

We need only recognize that ΔE_b is the number we have plotted vs. n, and $-\Delta H_d$ is the number Wall, et al., have plotted vs. $n^{2/3}$ to appreciate that there is an exact thermodynamic relationship between the two quantities, which is readily evaluated given the appropriate heat capacity and virial coefficient data.

While experimental data are not available for the higher members of the paraffin series, empirical expressions for heat capacities as functions of n and T have been published which allow an approximate calculation to be made. Huggins[6] gives an expression for the heat capacities of liquid paraffins as

$$C_p^1 = (6.57 + 0.033 \times 10^{-6}T^3)n$$

for T between 140 and 380°K. Edmister[13] provides an expression for gaseous paraffins

$$C_p^g = (2.56 + 0.51n) + (0.0042 + 0.0130n)T$$

For the paraffins with n greater than 10, the enthalpy of the vapor is essentially independent of pressure in the range of the calculation. For the lower paraffins a correction is necessary; the calculation is somewhat tedious, but it was done for hexane in order to extend the calculation into the range below $n = 11$. The second virial coefficient data of McGlashan and Potter[14] were used.

If we let $\Delta(PV)_b = RT_t$, we can evaluate $-\Delta H_d$ based on our values of ΔE_b. The results for four molecules are presented in Figure 2. Since the C_6 would not be expected to coil anyway, it is difficult to say which of the lines is more nearly linear; however, invoking the principle of greatest simplicity, there is no reason to use a two-thirds dependence when a linear one is adequate. Indeed, the work of Huggins[6] would predict such a dependence were it not for his acceptance of the coiling concept. In addition, Bradley and Shellard[15] have claimed that the enthalpy of vaporization of the paraffins follows a linear rather than a two-thirds power dependence on n. In order to resolve the discrepancy, we have examined the heats of vaporization of the paraffins from C_9 to

(13) W. C. Edmister, Ind. Eng. Chem., 30, 352 (1938).
(14) M. L. McGlashan and D. J. B. Potter, Proc. Roy. Soc., Ser. A, 267, 478 (1962).
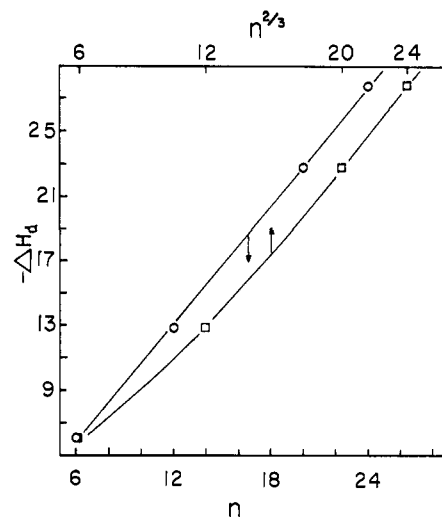(15) R. S. Bradley and A. D. Shellard, ibid., Ser. A, 198, 239 (1949).

Figure 2. Enthalpy of vaporization at 100° calculated from energy of vaporization at "corresponding" temperatures plotted vs. n and $n^{2/3}$ (see text).
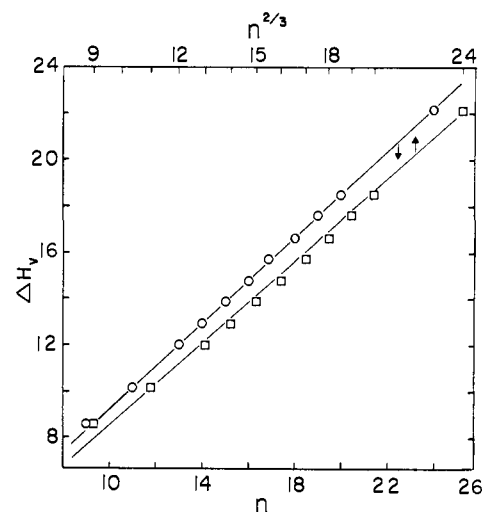

Figure 3. Enthalpy of vaporization at 200° for the normal paraffins, calculated from Antoine equations (see text). There is a slight but definite curvature to the points when plotted vs. $n^{2/3}$.

C_{20} at 200° based on the vapor pressures of Rossini and coworkers,[12] and for C_{24} based on our own data produced with the same technique they used. These data should be very self-consistent and provide a better analysis of the dependence of enthalpy of vaporization on n than data taken from different sources.

Compressibility corrections were applied using the same reference that Wall, et al.,[7] used, yet the plot of enthalpy of vaporization vs. n is quite linear (see Figure 3). A possible explanation for the conclusions of Wall, et al., is that their vapor pressure data are from inconsistent sources.

The question now arises whether the linear dependence of ΔE_{vap} on n at "corresponding" temperatures (equivalent to the linear dependence of ΔH_{vap} on n at constant temperature by the above analysis) excludes the possibility of coiling of vapor-phase molecules. The observation that each carbon contributes a fixed amount to the energy of vaporization from C_5 to C_{24} certainly indicates that there are no carbons buried inside of a coil wherein significant amounts of

intramolecular energy exist. A linear dependence of vaporization energy on n would be expected if the vapor molecules coiled into cylindrical helices with a fixed surface area exposed per carbon atom in the chain. However, there is no break in the linearity between C_4, which cannot form a helix, and the rest of the higher paraffins, which sooner or later could be expected to form one. Furthermore, the absolute entropy increment between C_4 and C_5, C_5 and C_6, etc., is the same, indicating no specific restrictions up to C_8 in the gas phase. (This observation cannot be tested for the higher members of the series, since for these molecules the data in the API Tables are *based* on a constant entropy increment, not on experimental data. This situation should be rectified.) We conclude that energetically favored coiling of vapor-phase molecules does not occur in the temperature range of our studies for paraffins up to C_{24}.

It must be noted that the values of enthalpy of vaporization predicted by the $n^{2/3}$ dependence of Wall, *et al.*,[7] are much closer to their observed values for C_{24}, C_{36}, and C_{94} than those predicted by a linear dependence on n (see Table III). This observation may

Table III. Comparison of ΔH_{vap} Predicted from $n^{2/3}$ and n^1 with Measured Values

n	kcal/mol			T, °C
	ΔH_{meas}	$\Delta H_{2/3}{}^a$	ΔH_{lin}	
24	21	21.9		75
			21.5	200
36	29	28.6		145
			33.2	200
94	46	55		345
			86.8	200

[a] Wall, *et al.*[7]

be a consequence of the method used to measure the enthalpy of vaporization, namely, through rates of molecular vaporization (the Langmuir technique). Because the molecules are pumped away immediately after leaving the liquid, the equilibrium configuration of the vapor-phase molecules can play no role in determining the derived enthalpy of vaporization. If in fact a molecule leaves the liquid in a tightly coiled configuration and exists in a loose, random configuration in the equilibrium vapor, the enthalpy of vaporization so derived will be smaller than that based on equilibrium vapor pressure data by an "enthalpy of uncoiling."

Because of the large discrepancy in temperature between the data of Wall, *et al.*[7] (75°), and the present work (200°) it is difficult to estimate a value for this quantity for *n*-tetracosane at either temperature. Based on the evidence presented in this paper, we con-

clude that the "enthalpy (or energy) of coiling" at 200° is sufficiently small to be overcome by the entropy advantage of a loose, random configuration. It is quite possible that this situation may not obtain at lower temperatures, however, and at 75° the *n*-tetracosane molecule may in fact exist as a tight, energetically favored "sphere" in the vapor phase.

In order to examine this possibility, enthalpies of vaporization at lower temperatures should be obtained with a Knudsen technique for comparison with those obtained by the Langmuir technique.[16] It is well known that vapor pressures measured with the latter technique are not necessarily equilibrium values; a difference in the derived enthalpies may be considered an "energy of coiling."

The calculation of Langmuir[4b] mentioned at the beginning of this paper led to an energy of coiling of 8 kcal/mol at 25°C. (He used a surface energy of 50 cm/dyn and a surface area difference of 116 Å^2 between coiled and uncoiled palmitic acid molecules.) If indeed this much energy is given up on coiling, the molecule would certainly coil up at 25°. In order to evaluate this type of calculation, we have repeated it for *n*-tetracosane, using molecular properties appropriate to a temperature of 200°. From our surface tension data, we predict a value of 51 cm/dyn for the surface energy; using data in the paper of Orwoll and Flory,[11] the density is 0.682 g/ml. This leads to a surface area difference of 268 Å^2, which in turn corresponds to an energy of coiling of 20 kcal/mol.

To produce an equilibrium constant of 10 in favor of the uncoiled form of the molecule at 200°, the entropy difference between the two forms would have to favor the uncoiled form by a factor of 10^{10}. This great a probability advantage does not seem likely, so the calculation predicts energetic coiling even at 200°.

Since we claim that the molecule does not coil energetically at 200°, we must question the value of Langmuir's calculation, even at 25°. Perhaps the overestimate of the coiling energy arises from the application of a surface energy, a property of many molecules acting in concert, to a single molecule.

The most obvious piece of evidence required in a discussion of vapor-phase coiling is an experimentally measured absolute entropy for a long-chain molecule at 298.16°K in the ideal gas state. This is unfortunately not presently available.

Conclusion. There is no evidence in the literature that long-chain vapor-phase hydrocarbons coil up into energetically favored spheres or helices. We have provided evidence that no such coiling occurs in molecules up to and including 24 carbons in length.

(16) See, *e.g.*, R. C. Paule and J. L. Margrave in "The Characterization of High Temperature Vapors," J. L. Margrave, Ed., Wiley, New York, N. Y., 1967, p 130.