CONTINUUM REACTION FIELD CALCULATION OF DIELECTRIC CONSTANT AND VAPOR PRESSURES FOR WATER AND CARBON DISULFIDE

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ABSTRACT Continuum reaction field theory is applied to calculations of dielectric constant, contribution of intermolecular interactions to the free energy of a liquid, and heat of vaporization. Introduction of repulsive interactions and the use of one adjustable parameter, the free volume, enables prediction of vapor pressures. The calculations are illustrated for a simple nonpolar liquid, carbon disulfide, and for liquid water. It is shown that when Onsager's equation is rearranged to a quadratic equation, and a recently found value of the polarizability is employed, its solutions for liquid water yield good agreement with experimental values throughout the whole temperature range. The decrease of the dielectric constant with temperature is essentially linear with the inverse of absolute temperature, but there is additional significant decrease due to the decrease of density with temperature. The relatively high value of the heat of vaporization of liquid water is expressed in terms of large dipolar interaction of a water molecule with the environment, which is due to polarization effects.

I. INTRODUCTION

This study presents a simple method for calculating the contribution of intermolecular interactions to the free energy of a liquid with the method of continuum reaction field theory. The attractive interactions which will be considered are dispersion interactions and dipolar interactions of a polarizable molecule embedded in a cavity with the entire environment. Previous attempts to obtain the heat of vaporization with the continuum reaction field approach (1) resulted in reasonable agreement with experiment. This was an indication that in the case of simple liquids the model was applicable in accounting for intermolecular interactions, at least as a first order approximation. In the cases considered in ref. 1 dispersion interactions gave the dominant contribution to intermolecular interactions. In the present work, further developments in the application of the method are introduced, and the calculations on liquid water illustrate the importance of the dipolar term.

It has to be noted that in the calculation of both components of attractive interactions no adjustable parameters are used. For the purpose of accounting for the incompressibility of liquids repulsive interactions will also be introduced. An introduction of repulsive interactions of exponential form, which is widely used, and the use of an adjustable parameter, the free volume, enables an extension of the treatment for the prediction of vapor pressures at various temperatures.

The calculations will be illustrated for the case of two liquids, (*a*) carbon disulfide, which stands for a simple nonpolar liquid, and (*b*) liquid water, which is a complex polar liquid. One reason for the choice of liquid water was the availability of extensive data. Another reason was the interest in the study of liquid water itself.

We will show that two of the anomalies attributed to liquid water, its high dielectric constant, ϵ, and its high heat of vaporization are explained in the framework of the reaction field theory, whose static part is the Onsager theory (2), provided that parameters obtained from refractive index data, including the infrared region are employed. In calculating the dielectric constant, we employ a value of the static polarizability, which accounts for atomic and molecular motions, and is 2.8 times larger (3, 4) than the previously used value, which only takes into account electronic motions. The previous application of the Onsager (2) equation to the case of liquid water resulted in an underestimate of the dielectric constant (30 instead of 80) when the vapor value for the permanent dipole moment was employed, or in an overestimate of the value of the permanent dipole moment (5) (3×10^{-18} esu instead of 1.84–1.85×10^{-18} esu) when the experimental value of the dielectric constant was used.

This discrepancy led to a criticism of the Onsager theory and to the development of a more general theory (6–8) for the dielectric constant. In parallel with this development various structural models (9–13) have been employed to calculate the dielectric constant of liquid water. Both approaches have improved the agreement with experiment of calculated dielectric constants, but it was realized that the results were far from being satisfactory.

The main point of criticism of the Onsager theory has been its apparent neglect of effects of short range intermolecular forces (6, 8). The results of the present work would imply that perhaps the effects of short range intermolecular forces are partly included in the reaction field treatment through the values of the densities and polarizabilities. The atomic and molecular contributions to the polarizability may depend on the molecular environment, which follows from the fact that several infrared bands in the liquid state of water are absent in its vapor.

It should be acknowledged that the idea that the Onsager theory for the dielectric constant may be applicable to the case of liquid water has already been expressed by Hill (14, 15) who replaced the "internal refractive index," n^2, in the visible by a higher value of its extrapolation in the microwave region (*vide infra*). Our treatment is slightly different, making use of the value of the polarizability, which leads to a further improvement of the agreement with experiment for the whole temperature range.

In section II we employ Onsager's theory to calculate the permanent dipole moment of liquid water. In section III we will discuss the temperature dependence of the dielectric constant as given by the Onsager theory and will present results of calculation on water. In section IV we will present the calculations of free energy due to intermolecular interactions and calculations of the heat of vaporization of carbon disulfide and liquid water with the reaction field theory. In section V we will introduce repulsive interactions and will calculate vapor pressures.

II. CALCULATION OF THE PERMANENT DIPOLE MOMENT OF LIQUID WATER WITH ONSAGER'S EQUATION

Following Bottcher (5), Onsager's equation for the case of a pure liquid can be written in the form

$$(\epsilon - 1)(2\epsilon + 1)/12\pi\epsilon = [N\alpha/(1 - f\alpha)] + [N\mu^2/(1 - f\alpha)^2 3kT], \qquad (1)$$

in which f is the factor of the reaction field,

$$f = (1/a^3)[(2\epsilon - 2)/(2\epsilon + 1)], \qquad (2)$$

and a is given by

$$(4\pi/3)Na^3 = 1. \qquad (3)$$

N is the number of molecules per unit volume, α is the polarizability, μ is the permanent dipole moment, k is Boltzmann's constant, and T is the absolute temperature.

When Eqs. 1-3 are used for the case of liquid water, using $\alpha = 1.45 \times 10^{-24}$ cm^3 (refs. 13, 16) (at $t = 20°$C, $\epsilon = 80.4$) it turns out that μ is approximately 3×10^{-18} esu.

Recently we developed a semiempirical procedure (3, 4, 17) for obtaining the representation of the refractive index as a function of the frequency (w) of the electromagnetic field. The theory is based on the model of bound and damped oscillators and is described in ref. 18. For the purpose of the application in section IV we present a description of the procedure (see ref. 4 for more detail). The basic equations we employ are:

$$[\bar{n}^2(w) - 1]/[\bar{n}^2(w) + 2] = (4\pi/3)N\alpha(w) = \beta(w), \qquad (4)$$

and

$$(4\pi/3)N\alpha(w) = \sum_{i=1}^{P} C_i/[1 - (w/w_i)^2 - i\gamma_i w/w_i^2], \qquad (5)$$

in which w_i is an absorption frequency and γ_i is a damping factor; $\bar{n}$ is the complex refractive index given by

$$\bar{n}(w) = n(w) + ik(w), \qquad (6)$$

in which the real part, $n(w)$, is the ordinary refractive index; C_i is a coefficient proportional to the oscillator strength f_i;

$$C_i = 4\pi N f_i e_i^2/3w_i^2 m_i, \qquad (7)$$

where e_l and m_l stand for the charge and mass of the oscillator, respectively. For molecules possessing permanent dipole moments Eq. 4 is applicable only at sufficiently high frequencies, i.e., when the permanent dipole moments cannot follow the rapidly oscillating electromagnetic fields. For liquid water we used Eq. 4 at wavelengths shorter than 10^{-2} cm. In our procedure we used a least-squares fit for the real part of Eqs. 4 and 5. These equations represent a set of m linear equations in the C_l's where m, the number of measurements of $\bar{n}(w)$, is much larger than P, the number of absorption frequencies (bands) employed. The γ_l's may be regarded as parameters, or, alternatively, are set equal to the band widths. When the C_l's are known the polarizability extrapolated to infinite wavelength is also known according to the relations

$$\alpha(0) = \sum_{l=1}^{P} \alpha_l(0), \tag{8}$$

and

$$\alpha_l(0) = 3C_l/4\pi N. \tag{9}$$

The procedure has already been applied for hydrogen, oxygen, and water in both the gaseous and liquid states, and for carbon dioxide and monoxide, carbon disulfide, benzene, glass and to solutions (19). In all cases a good agreement between calculated and observed $n(w)$ was obtained, in most cases significantly better than according to previous dispersion formulas. The calculations on liquid water, where four infrared bands and one ultraviolet band have been considered, yielded values of the polarizability $\alpha(0)$ significantly larger than previously recorded. When data on $k(w)$ are included we obtain $\alpha(0) = 4.04 \times 10^{-24}$ cm^3, whereas neglecting $k(w)$ leads to $\alpha(0) = 3.95 \times 10^{-24}$ cm^3. Both results are appreciably larger than the previously used value (16), $\alpha = 1.45 \times 10^{-24}$ cm^3, which was determined by ignoring the infrared bands in extrapolating from the visible and ultraviolet regions towards infinite wavelengths. The extrapolation to $w = 0$ of the ultraviolet and visible contribution to $\alpha(w)$, leads to the same value for both the liquid and gaseous states of water, which also coincides with the previously obtained value (16). This part of α may be interpreted as due to electronic motions. The large value of the static polarizability of liquid water is due to the first two infrared bands which are interpreted as arising from intermolecular motions (20) and might be due to the hydrogen bonds in the structure of liquid water (Table I).

Making use of Eqs. 3–5 we obtain: for $\alpha = 4.04 \times 10^{-24}$ cm^3, $\mu = 1.70 \times 10^{-18}$ esu for $\alpha = 3.95 \times 10^{-24}$ cm^3, $\mu = 1.75 \times 10^{-18}$ esu.

These values are close to the vapor value $\mu = 1.84 \times 10^{-18}$ esu and are well within the range of values obtained from dilute solutions of water in nonpolar liquids, $\mu = 1.7 - 1.9 \times 10^{-18}$ esu (see ref. 21, p. 31).

III. TEMPERATURE DEPENDENCE OF THE DIELECTRIC CONSTANT

In order to study the predictions of the Onsager theory for the temperature dependence of the dielectric constant at different temperatures, we first make use of Eqs. 2 and 3

TABLE I

ABSORPTION WAVELENGTHS AND BAND CONTRIBUTION TO THE STATIC POLARIZABILITY OF WATER

Substance	Absorption wavelength	$\alpha_i(0)$ contribution to static polarizability ($\times 10^{-24}$ cm^3)
	μm	
Liquid water (t = 20°C, data on $k(w)$ included in calculations), $\alpha = 4.04 \times 10^{-24}$ cm^3	51.8	1.10
	14.3	1.33
	6.08	0.03
	2.86	0.14
	0.099	1.44
Liquid water (t = 20°C, data on $k(w)$ not included in calculations) $\alpha = 3.95 \times 10^{-24}$ cm^3	51.8	1.11
	14.3	1.23
	6.08	0.03
	2.86	0.14
	0.099	1.44
Gaseous water (t = 0°C)	0.099	1.456

and rearrange Eq. 1 from an apparently cubic equation to a quadratic equation in ϵ,

$$A\epsilon^2 - B\epsilon - C = 0, \tag{10}$$

in which $A = 2(3 - 4\pi N\alpha)^2$, $B = (36\pi N\mu^2/kT) + (3 + 8\pi N\alpha)(3 - 4\pi N\alpha)$, and $C = (3 + 8\pi N\alpha)^2$.

Note that in the absence of a permanent dipole, or at optical frequencies, when the permanent dipole moments cannot follow the oscillating fields, Eq. 10 is reduced to the Lorentz-Lorenz equation, Eq. 4, which is used in our procedure for obtaining the polarizability from refractive index data. Although no approximation is needed for the solution of Eq. 10 it is instructive to consider it for the case A, C, $\ll B$, where to first order of approximation,

$$\begin{aligned} \epsilon &= B/A, \\ &= \frac{18\pi N\mu^2}{kT(3 - 4\pi N\alpha)^2} + \frac{1}{2}\,\frac{1 + 8\pi N\alpha/3}{(1 - 4\pi N\alpha/3)}. \end{aligned} \tag{11}$$

From inspection of Eq. 11 it follows that if changes in density with temperature may be ignored ϵ decreases linearly with $1/T$. However, the decrease of the density with temperature introduces another effect which might be of importance. For instance, in the case of liquid water where the density at 95°C is 4% less than its value at 20°C, this effect introduces an additional decrease of more than 10% in the value of ϵ at 95°C, relative to its value at 20°C.

As was pointed out in section I the idea that the Onsager theory is satisfactory for the case of liquid water has already been expressed by Hill (14, 15) who replaced n^2 by ϵ_∞ in the following equation,

$$(\epsilon - n^2)(2\epsilon + n^2)/\epsilon(n^2 + 2)^2 = 4\pi N\mu^2/9kT. \tag{12}$$

ϵ_∞ is the high-frequency limit of ϵ which is used to fit the experimental results in the microwave region. Hill (14) employed the two values: $\epsilon_\infty = 5$ and $\epsilon_\infty = 4.5$, resulting in values for μ between 1.68 and 1.61 and between 1.83 and 1.76, respectively, in the temperature range 0–50°C. However, the temperature dependence of ϵ_∞ should not be neglected. If one assumes α to be temperature independent and uses the relation

$$\epsilon_\infty = [1 + (8\pi/3)N\alpha][1 - (4\pi/3)N\alpha], \qquad (13)$$

then due to change in density, ϵ_∞ in the case of liquid water should decrease with temperature by about 10% throughout the temperature range 0–100°C. A significant improvement in the agreement with experiment at temperatures between 0 and 60°C was obtained by Hill (15) when using values of ϵ_∞ which decrease with temperature from 4.35 at 0°C to 4.05 at 60°C. In passing we will point out that this temperature dependence of ϵ_∞ is compatible with Eq. 13 and with the assumption of temperature independence of the polarizability for this temperature range.

The neglect of the temperature dependence of the polarizability is not an essential part of the procedure outlined in this section. In fact, the procedure outlined in Eqs. 4–6 (see ref. 4) has to be repeated at various temperatures, thus yielding the polarizability at any desired temperature directly or by an interpolation.

Calculations on Liquid Water

It should be pointed out that in this study the polarizability was assumed to be temperature independent, following the procedure in previous studies (2, 5–7, 13, 22) on the dielectric constant. There is a host of experimental data (3–5, 21, 22) which indicates that the electronic contribution to the polarizability is essentially temperature independent.

In the case of liquid water the specific refraction, $[(n^2 - 1)/(n^2 + 2)](1/d)$, at the sodium D line varies from 0.206254 at 0°C to 0.205919 at 60°C (23) (d is the density).

The temperature dependence of the contribution of infrared bands to the polarizability has not yet been studied. There have been studies which indicate temperature dependence of the infrared absorption bands (24–26). Walrafen (25) has reported a substantial decrease with temperature in the integrated intensity of the far infrared bands of liquid water. Therefore it may be anticipated that the polarizability of liquid water is a decreasing function of temperature. However, the magnitude of this decrease should be directly investigated by performing refractive index measurements.

The calculated and observed values of $\epsilon(T)$ are given in Table II. In column 3 the values $\alpha = 3.95 \times 10^{-24}$ cm^3 and $\mu = 1.75 \times 10^{-18}$ esu are used in the calculations. In column 4 we present results which are obtained by using the vapor value for μ, i.e., $\mu = 1.84 \times 10^{-18}$ esu, where the value for α is obtained from Eq. 10 at 20°C ($\alpha = 3.77 \times 10^{-24}$ cm^3), and is in agreement within the uncertainty (about 5%) with the larger value.

A comparison of calculated with experimental values of ϵ at temperatures between 0 and 100°C indicates a good agreement. The differences between calculated and

TABLE II

CALCULATIONS OF DIELECTRIC CONSTANT OF LIQUID WATER AT DIFFERENT TEMPERATURES WITH ONSAGER'S THEORY

t	ϵ(obs)*	ϵ(calc) $\mu = 1.75 \times 10^{-18}$ esu, $\alpha = 3.95 \times 10^{-24}$ cm^3	ϵ(calc) $\mu = 1.84 \times 10^{-18}$ esu, $\alpha = 3.77 \times 10^{-24}$ cm^3
°C			
0	88	86.6	85.8
5	86	85.1	84.6
10	84.1	83.4	83.2
20	80.4	80.4†	80.4§
25	78.5	78.7	78.1
30	76.7	77.1	76.8
40	73.3	73.9	73.5
50	69.9	70.7	70.4
60	66.7	67.5	67.3
70	63.7	64.5	64.4
80	60.8	61.5	61.5
90	58	58.6	58.6
100	55.3	55.8	55.8

*Values of dielectric constants and densities of liquid water are taken from Handbook of Chemistry and Physics, The Chemical Rubber Co., 50th edition (1969–70).

†The value of ϵ at 20°C was used to determine μ.

§The value of ϵ at 20°C was used to determine α.

observed values of ϵ are about 1% and are in most cases within the experimental uncertainty. The agreement with experiment is somewhat better than that obtained in ref. 15. This might be attributed to the higher precision of refractive index measurements compared with microwave measurements of the real and imaginary parts of the dielectric constant.

If the polarizability of liquid water is a slightly decreasing function of temperature, the calculated values of ϵ will further decrease with temperature at temperatures above 20°C and will further increase at temperatures below 20°C so that the agreement of the calculated values with the experimental values might be found to be even closer.

IV. APPLICATION OF CONTINUUM REACTION FIELD TO CALCULATION OF FREE ENERGY OF INTERACTION

The continuum reaction field approach considers a given molecule in a liquid to be embedded in a cavity in a uniform surrounding dielectric. This starting point is identical with that of the Onsager (2) approach, whose equations for the dielectric constant and reaction field have been presented in previous sections. The method attempts to account for the interaction of a given molecule with the entire surrounding. The electrostatic part (orientation and induction effects) was developed by Martin (27) and Bell (28) and improved by Kirkwood (29) and Bonnor (30).

The contribution of the electrostatic (dipolar) interaction to the molar Helmholtz free energy in the liquid, F_{es}, is (5)

$$F_{es} = -\tfrac{1}{2}[f\mu^2 N_A/(1 - f\alpha)], \tag{14}$$

in which N_A is Avogadro's number and the other quantities appearing have been defined in Eqs. 1–3. The dispersion part was developed by Linder (1, 31–33) in a series a papers, in the first two of which (1) he also presented the calculation of energy of vaporization for several liquids and obtained a reasonably fair agreement with experimental values. In this section we will employ the version developed by Linder (33) who has also taken into account thermodynamical fluctuations according to the approach of Callen and Welton (34). Following Linder (33) the expression we employ for calculating the molar free energy of attractive intermolecular interactions according to the continuum reaction field theory is

$$F_{att} = N_A\left[-\frac{1}{2}\,\frac{f\mu^2}{(1 - f\alpha)} - \frac{3}{2}\,kT\sum_{n=0}^{\infty} f(i\xi_n)\alpha(i\xi_n)\right], \tag{15}$$

in which the term $n = 0$ is given half weight, and

$$\xi_n = 2\pi nkT/\hbar$$

($\hbar$ is Planck's constant divided by 2π) has the meaning of circular frequency and is analogous to w in Eqs. 4–7. Eq. 15 is obtained by decomposing the contribution to F into a dipolar part as in Eq. 14 and adding to it the dispersion part, which is obtained from Linder (33) (Eq. 146) by identifying the generalized susceptibility $x(i\xi_n)$, with the polarizability $\alpha(i\xi_n)$. Alternatively, the same expression is obtained by considering the above-mentioned equation as representing the total interaction per molecule and reinterpreting the generalized susceptibility at $\xi = 0$ according to the definition of Callen and Welton (34) and according to Onsager's (2) equations.

The terms Helmholtz free energy or Gibbs free energy can be used interchangeably in a liquid at a pressure below several atmospheres, since the product of the pressure with the molar volume, Pv, which is of the order of calorie per mole is much smaller than the magnitude of F_{att} in Eq. 15, which is of the order of several kilocalories per mole. In the calculations we have employed the relation

$$f(i\xi_n) = \{[2\epsilon(i\xi_n) - 2]/[2\epsilon(i\xi_n) + 1]\} \cdot (1/a^3). \tag{16}$$

Since for $n \geq 1$ $\epsilon(i\xi_n) = \bar{n}^2(i\xi_n)$ (ξ_1 is a circular frequency in the infrared) Eqs. 4 and 5 were employed, so that

$$F_{att} = -N_A\left[\frac{f\mu^2}{2(1 - f\alpha)} + \frac{3}{4}\,kTf\alpha + 3kT\sum_{n=1}^{\infty}\frac{\beta^2(i\xi_n)}{1 + \beta(i\xi_n)}\right]. \tag{17}$$

The first term in Eq. 17, which vanishes unless permanent dipoles are present, has been called a dipolar term, whereas the last term is a dispersion term. For a nonpolar liquid the second term corresponds to $n = 0$ in the dispersion summation.

For a polar liquid there may be two interpretations how to calculate this term. If we obtain Eq. 15 by adding dispersion interactions to Eq. 14 then $f(0)$ should be obtained by extrapolating the refractive index to zero frequency in Eq. 16. We calculated

TABLE III

CONTRIBUTION OF VARIOUS TERMS TO F_{INT} FOR LIQUID WATER AT 20°C*

Term	Contribution to F_{int}
	Kcal/mol
Dispersion	
$n = 1, 10, \xi_1 = 2.44 \times 10^{14}$ rad/s	−0.615
$n = 11, 100, \xi_{100} = 2.44 \times 10^{16}$ rad/s	−2.333
$n = 101, 1000, \xi_{1000} = 2.44 \times 10^{17}$ rad/s	−0.392
$n = 1001, 2500, \xi_{2500} = 6.11 \times 10^{17}$ rad/s	−0.0008
Dispersion (total)	−3.339
"Induction"	−0.213
Dipolar (electrostatic)	−6.513
Total F_{att}	−10.065

*The values of μ and α used in the calculations were 1.84×10^{-18} esu and 3.77×10^{-24} cm^3, respectively, corresponding to column 4 in Table II. The value of the coefficient C_{uv} at 20°C was 0.199, as in Table I, whereas the values used for the infrared coefficients are taken as 0.132, 0.146, 0.0019, and 0.018, which yield, according to Eqs. 8 and 9 the value of 3.77×10^{-24} cm^3 for α. The values of the coefficients C_i at other temperatures were obtained from the above coefficients by multiplications with $N(t)/N$ (20°C).

$f(0)$ in the second term according to Eq. 2, by starting from the generalized expression of Linder (33) (Eq. 146), in which we identified the generalized susceptibility $x(0)$ with $[(\mu^2/3kT)/(1 - f\alpha)] + \alpha$. Since in this case f depends on permanent dipole moments we have designated it as an "induction" term. It should be recognized that (*a*) the dipolar term also includes induction effects and (*b*) the "induction" term does not vanish in the absence of permanent dipoles, but becomes a part of the dispersion term. Our calculation of f according to Eq. 2 instead of from the extrapolated refractive index amounts, in the case of liquid water, to an increase of 30% in the magnitude of the second term. However, in any case the magnitude of the second term is a small fraction of that of the dispersion or dipolar terms, (see Table III) in analogy with the situation in gases (16), so that the distinction between the two versions is not critical.

Table III also illustrates the contribution of different spectral regions to dispersion interactions. We have included 2,500 terms although in practice the series has converged with 1,000 terms. Most of the contribution arises from the visible and ultraviolet regions. The practical implication of this analysis is that for the purpose of calculating dispersion interactions the absence of refractive index data in the infrared region is not crucial. Note that the value of $\beta(i\xi_n)$ in the visible and ultraviolet regions is almost independent of infrared terms. This means that for nonpolar liquids neglect of consideration of the infrared region will not result in an appreciable error in calculations of intermolecular interactions.

The results in Table III illustrate that in the case of liquid water the dipolar term is about two times larger than the dispersion term. The large magnitude of the dipolar

TABLE IV

CALCULATED VALUES OF FREE ENERGIES OF INTERACTION: COMPARISON OF CALCULATED WITH OBSERVED VAPOR PRESSURES

t	F_{att}	F_{int} (total)	P_{obs}	P_{calc}
°C	*Kcal/mol*		*mm Hg*	
Liquid water*				
15	−10.08	−7.93	12.79	13.3
20	−10.06	−7.92	17.53	17.5†
40	−9.94	−7.84	55.32	50.3
60	−9.75	−7.72	149.4	135
80	−9.52	−7.57	355.1	339
100	−9.27	−7.41	760	790
Carbon disulfide§				
−73.8	−9.30	−5.26	1	0.9
−44.7	−8.83	−5.04	10	9
−22.5	−8.47	−4.87	40	36
−5.1	−8.18	−4.74	100	92
25	−7.70	−4.51		353
28	−7.65	−4.49	400	400†
46.3	−7.38	−4.36	760	777

*The values of μ and α used in the calculations were 1.84×10^{-18} esu and 3.77×10^{-24} cm^3, respectively.

†The above value of P_{obs} was used in solving for F_{repul}.

§The values of the parameters C_i and W_i are taken from ref. 3 at 25°C. The density of carbon disulfide is taken from International Critical Tables, 1928. McGraw-Hill, New York. Vol. III: 23.

term arises not only because of the permanent dipole moment but also because of the polarizability. A neglect of the contribution of infrared bands to the static polarizability will reduce the dipolar term by about a factor of two.

In Table IV we present results of F_{att} (or G_{att}) for liquid water and CS_2 at various temperatures and at atmospheric pressure. In the calculations the temperature dependence of polarizability was ignored. The quantity $\beta(\xi, T)$ was obtained from $\beta(\xi, T_i)$ at T_i from the relation $\beta(\xi, T) = \beta(\xi, T_i)N(T)/N(T_i)$, in which T_i = 20°C for liquid water and T_i = 25°C for CS_2.

Heat of Vaporization

In the following we will employ the "subscript "int," to designate the sum of attractive and repulsive intermolecular interactions.

The purpose of the following discussion is to illustrate how to obtain the heat of vaporization from a knowledge of F_{int}. However, in the calculations we will consider only F_{att}, which implies that a rough estimate of the heat of vaporization can be obtained from the attractive interactions alone, which have been obtained without any introduction of adjustable parameters.

The calculations of Linder (1) and those presented here neglect the change in the contribution of internal degrees of freedom to the internal energy when going from the liquid to the vapor. Hence the discontinuous jump in internal energy upon vaporization is attributed to the change in the magnitude of intermolecular interactions. At pressures of several atmospheres and lower, the intermolecular interactions in the vapor can be neglected compared with those in the liquid so that

$$\Delta U \text{ vaporization} \approx -U_{\text{int}}(\text{liq}) \tag{18}$$

and the heat of vaporization

$$\begin{aligned} \Delta \text{H vaporization} &= \text{H gas} - \text{H liquid}, \\ &= RT - \text{U}_{\text{int}}(\text{liq}) - Pv(\text{liq}), \end{aligned} \tag{19}$$

in which the term $Pv(\text{liq})$ may be neglected at pressures of several atmospheres or below.

The value of H_{int} (liq) is obtained by

$$\begin{aligned} H_{\text{int}}(\text{liq}) &= G_{\text{int}} + S_{\text{int}} T, \\ &= G_{\text{int}} - (\partial G_{\text{int}}/\partial T)|_P T, \end{aligned} \tag{20}$$

or alternatively from

$$U_{\text{int}} = F_{\text{int}} - (\partial F_{\text{int}}/\partial T)|_v T. \tag{21}$$

Since the density and dielectric constants in our case are known at atmospheric pressure we preferred to use Eq. 20 with the approximation

$$\begin{aligned} H_{\text{int}} = H_{\text{int}}(T, P_o = 1 \text{ atm}) &= G_{\text{int}}(T, P_o) \\ &- T \lim_{\Delta T \to 0} [G(T + \Delta T, P_o) - G(T, P_o)]/\Delta T, \\ &\approx G_{\text{int}}(T, P_o) - T(\Delta G/\Delta T)(T, P_o). \end{aligned} \tag{22}$$

In calculating H_{int} it should be realized that a relatively small error in $\Delta G/\Delta T$ may result in a large error in H_{int}. For instance, an error of 0.01 Kcal/mol degree will result in an error of 3.7 Kcal/mol in H_{int} (100°C, P_o). In view of this sensitivity and the fact that the parameters for liquid water (in Table I) were available only at 20°C, the calculated values of H_{int} for liquid water are reliable only at 20°C.

From Table IV it is seen that G_{int} (or G_{att}) is an increasing function of temperature (i.e. its magnitude decreases with temperature) and therefore S_{int} (or S_{att}) is a negative quantity, which makes the absolute magnitude of H_{int} larger than that of G_{int}. In the case of liquid water the magnitude of S_{att} (20°, P_o) turns out to be -4 e.u. from which the heat of vaporization, ΔH vaporization (20°C, P_o) $= RT - G_{\text{att}}$ (20°C, P_o) $- S_{\text{att}}\, T$ turns out to be 11.8 Kcal/mol. The experimental heat of vaporization, at 20°C is (35) 10.5 Kcal/mol. Hence, the above calculation overestimates the heat of vaporization by 11%, which may be regarded as a reasonable agreement. If the value of S_{att} is calculated at 100°C, the calculated value of the heat of vaporization at 100°C becomes 14.5 Kcal/mol, whereas the experimental value is 9.7 Kcal/mol.

This discrepancy is attributed to the sensitivity of the calculated heat of vaporization to the temperature dependence of G, together with absence of sufficiently detailed information on the parameters of liquid water at 100°C. If the value of S_{att} at 20°C is used, the result would be 11.5 Kcal/mol, i.e. less than the value at 20°C, in qualitative accord with the decrease of the heat of vaporization with temperature.

In the case of CS_2 the absolute magnitude of F_{att} at 25°C, +7.7 Kcal/mol, already exceeds the heat of vaporization, which is (35) 6.7 Kcal/mol. From consideration of attractive interactions only, the calculated heat of vaporization for CS_2 at 25°C turns out to be approximately 12 Kcal/mol. In the two cases presented, the quantity S_{att} is negative, corresponding to the ordering introduced by intermolecular interactions. The absolute values of F_{att} or G_{att} are close to the values for heats of vaporization, but the addition of the term $-S_{att}T$ leads to an overestimate, which in the cases treated varies between 10% and 80%. In part this overestimate is a result of the fact that relatively small errors in the calculation of $G_{att}(T)$ can result in large errors in the term $-S_{att}T$. However, these results also illustrate the need to introduce repulsive intermolecular interactions.

V. REPULSIVE INTERACTIONS AND CALCULATION OF VAPOR PRESSURE

An inadequacy of the expression of the free energy in section IV (F_{att}) is its lack of accounting for repulsive interactions, which prevent the liquid from being compressed. Consequently, the relation

$$(\partial F/\partial v)_T = -P \tag{23}$$

is not satisfied. We have introduced repulsive interactions in such a way that Eq. 23 be satisfied at each temperature.

Regarding the functional form of the repulsive interactions we will only report the results obtained with the use of an exponential potential, which stems from the form $A \exp(-\mu R)$, which incidentally was also chosen in another recent study on water (36). We express F_{repul} in the form

$$F_{repul}(T, v) = A(T)\exp(-C(v_m^{1/3} - v_{core}^{1/3})) \tag{24}$$

in which v_m is the volume per molecule, ($v_m = 1/N$), and v_{core} is the incompressible molecular volume. The coefficient C has been considered to be temperature independent. The expression for the total free energy function, F_{liq}, is given by

$$F_{liq} = -RT\ln g(\mathrm{int}) - RT\ln(V_F/N_A\lambda^3) + F_{int}, \tag{25}$$

in which $g(\mathrm{int})$ is the part of the partition function due to internal degrees of freedom, $\lambda = h/(2\pi mkT)^{1/2}$, m is the molecular mass, and V_F is the molar free volume. (In ref. 37 the assumptions leading to Eq. 25 are discussed.) F_{int} is given by

$$F_{int}(v, T) = F_{att}(v, T) + F_{repul}(v, T). \tag{26}$$

From the equilibrium relation for the chemical potentials

$$\mu(\text{gas}) = \mu(\text{liq}) \tag{27}$$

and by neglecting changes in the contribution of internal degrees of freedom to the free energy upon vaporization, it follows that

$$\overline{P} = (RT/V_F)\exp(G_{\text{int}}/RT), \tag{28}$$

where $\overline{P}$ is the vapor pressure of the liquid. It is worthwhile to point out that Eq. 28 may also be derived from general thermodynamical considerations, without making use of Eq. 25, in which case the term R/V_F will be replaced by some parameter. Consider the relation

$$\mathrm{d}\ln \overline{P}/\mathrm{d}T = \Delta\mathrm{H}\ \text{vaporization}/RT^2, \tag{29}$$

which is an approximate form of Clapeyron's equation.

From Eqs. (19) and (29) we obtain

$$\mathrm{d}\ln \overline{P}/\mathrm{d}T \approx (1/T) - (H_{\text{int}}/RT^2). \tag{30}$$

From the relation $H_{\text{int}} = -T^2(\partial/\partial T)(G_{\text{int}}/T)$ it follows that

$$\mathrm{d}\ln \overline{P}/\mathrm{d}T \approx (1/T) + (\partial/\partial T)(G_{\text{int}}/RT). \tag{31}$$

Integration of Eq. 31 readily yields Eq. 28, in which R/V_F is an integration constant. Hence, the form of Eq. 28 is quite general and does not require the specific form of Eq. 25 for F_{liq}. The fact that integration of Eq. 31 yields an apparent independence of V_F of temperature is merely a result of the neglect of terms of relatively small magnitude, e.g., Pv_{liq}. Since v_{liq} itself varies only slightly with temperature, we do not anticipate appreciable changes of V_F with temperature.

Since in Eq. 23 P is much smaller in magnitude compared with the terms on the left-hand side, Eq. 23 was solved by setting to zero the right-hand side. From Eqs. 23 and 15 we have determined the quantity $\frac{1}{3}v^{1/3}CF_{\text{repul}}$ at each temperature. More details are given in the Appendix. Hence, another equation was needed for the determination of F_{repul}. Thus Eq. 28 for the vapor pressure was used at one temperature. In order to apply Eq. 28 a choice had to be made for the value of V_F. In this work the free volume was assumed to be proportional to the total volume. Once the value of V_F at one temperature was chosen, the vapor pressure was calculated for the whole temperature range and the results were compared with the experimental values. Finally, the value of V_F which gave the overall best agreement between calculated and experimental values of vapor pressures was chosen. In Table IV we compare the experimental values of the vapor pressure with the calculated values. The good agreement obtained suggests that the temperature dependence of G_{int} is in accord with experiment. The prediction of vapor pressures provides another method to predict heats of vaporization from Eq. 29.

From Table IV it follows that the magnitudes of repulsive interactions in liquid water and carbon disulfide at atmospheric pressure are approximately 20% and 40%, respectively, of the magnitudes of attractive interactions. This illustrates that a rough idea about the magnitude of intermolecular interactions may be obtained from a consideration of attractive interactions alone.

The values of V_F which gave the best agreement between calculated and observed vapor pressures are 1.3 cm^3 for liquid water at 20°C, and 25 cm^3 for carbon disulfide at 25°C. As was shown in Eqs. 29–31 V_F can be regarded merely as a parameter. Interpretation and discussion of the various aspects of the concept of the free volume are given in ref. 38. Our interpretation of the free volume is according to the following relation

$$V_F = N_a(v_m - v_{\text{core}})\gamma, \tag{32}$$

in which γ is some geometrical factor smaller than unity, which reflects the fact that part of the volume in a liquid is inaccessible because of packing of incompressible units. The values of molar volumes in liquid water and carbon disulfide are ~18 cm^3 and 60 cm^3 at 20°C. Hence, it might be that the difference $v_m - v_{\text{core}}$ is several times smaller in water than in carbon disulfide. However, more cases should be studied before drawing any conclusions. In addition, the determination of V_F has not yet been optimized. In the case of carbon disulfide any value of V_F between 18 cm^3 and 30 cm^3 could yield an approximate prediction of vapor pressures, whereas in water the range varies between 1 and 2 cm^3.

VI. DISCUSSION

The results of this work present another illustration for the usefulness of the continuum reaction field theory (2, 31–33) for quantitative predictions of dielectric constants (2) and intermolecular interactions in liquids (1). It has to be realized that part of the complexity of intermolecular interactions has already been implicitly absorbed in the values of densities which are employed in the calculations. In the case of liquid water it may be that in addition the value of the polarizability arising from infrared bands is affected by the liquid environment. The basis for this possibility may be the fact that the large value of the static polarizability of liquid water is due to the first two infrared bands (see Table I), which are interpreted as arising from intermolecular motions (20). These bands are absent in the vapor state of water. However, refractive index data in the far infrared region are not available for the vapor, so that the difference between the polarizability in the liquid and the vapor can be speculated.

The magnitudes of the dielectric constant and intermolecular electrostatic interactions in liquids of large dielectric constant depend not only on the magnitude of the permanent dipole moment and on the number of molecules per unit volume but also critically on the polarizability. Consequently, the atomic and molecular contributions to the polarizability should be taken into account in dielectric constant and in free energy calculations.

It should be stressed that a comparison of the magnitude of dispersion interactions in liquid water with other liquids (1) does not indicate any anomaly for the case of liquid water. The magnitude of dispersion interactions depends on the density and on the part of the polarizability arising from visible and ultraviolet bands. The contribution of infrared bands to dispersion interactions is relatively small (see Table III). In this regard it is noteworthy that the magnitude of the polarizability arising from visible and ultraviolet bands is almost the same in the liquid and vapor states of water (3, 4) (see Table I).

The anomalous high value of the heat of vaporization of liquid water is due to the dipolar interaction with the polarizing medium. The treatment of the reaction field yields the high value of heat of vaporization of liquid water when the contribution of infrared bands to the polarizability is taken into account.

Repulsive interactions have to be introduced in order to satisfy the thermodynamic relation $(\partial F/\partial v)_T = -P$ and in order to account for the overestimate in the heat of vaporization when only attractive interactions are taken into account. The use of the above relation provides a simple procedure for the introduction of repulsive interactions, which employs a minimal number of assumptions and only one parameter, V_F, whose interpretation is still to be investigated from calculations on more liquids. The introduction of repulsive interactions significantly improves the estimate of heat of vaporization and enables the prediction of vapor pressures, and therefore also boiling temperatures.

In the present treatment a molecule in a liquid is embedded in a spherical cavity whose volume is $1/N$, and the permanent dipole moment resides at the center of the cavity. The success of the model may stimulate reconsideration of a shift of the permanent dipole moment from the center of the cavity, and a refinement of the concept of the cavity as well as varying its shape.

When the contribution, (which may be negative or positive) of higher moments to intermolecular interactions in liquids becomes known, it can be simply added to the present expression for F_{att} (or G_{att}).

Regarding the detailed structure of liquid water, the present treatment does not exclude the possibility of a mixture (10, 39) model for liquid water. However, we avoided in this framework the use of additional assumptions, e.g., the properties of the species which form the mixture in liquid water.

The degree of success of the application of the method for pure liquids may also provide an idea about the importance of various interactions in solutions. The coupling of free-space quantum mechanical calculations with continuum reaction field treatment of solvent effects may be a promising way of predicting conformations of molecules in various solvents (40, 41).

This work is an extended version of a previous article and a lecture given at the Biophysical Society symposium (42).

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APPENDIX

We discuss here the details of the determination of F_{repul}. From Eqs. 23–25 we have

$$-RT(\partial \ln V_F/\partial v) + (\partial F_{\text{att}}/\partial v) + (\partial F_{\text{repul}}/\partial v) = 0. \tag{33}$$

By making use of the relations

$$v_m = v/N_A, \text{ i.e., } \partial/\partial v = (1/N_A)(\partial/\partial v_m),$$

and by neglecting the dependence of v_{core} on v_m, we obtain

$$-RTv(\partial \ln V_F/\partial v) + v_m(\partial F_{\text{att}}/\partial v_m) = (C/3)v_m^{1/3}F_{\text{repul}} \tag{34}$$

Consider the left-hand side of Eq. 34 to be a given number, $B_1(T)$, i.e.,

$$B_1(T) = (C/3)v_m^{1/3}F_{\text{repul}}(T). \tag{35}$$

Since $B_1(T)$ is a known number at each temperature, a knowledge of C, which is assumed to be independent of temperature, suffices for the determination of F_{repul} at any temperature.

From Eq. 28 we have

$$RT\log(V_F\overline{P}/RT) = G_{\text{int}}, \tag{36}$$

which can be approximated by

$$RT\log(V_F\overline{P}/RT) - F_{\text{att}} = F_{\text{repul}}(T). \tag{37}$$

By using Eq. 37 at one temperature, T_1, and substituting the value of $F_{\text{repul}}(T_1)$ in Eq. 35 the unknown C is solved. In the following we will calculate the contribution to the term $v_m(\partial F_{\text{att}}/\partial v_m)$.

The derivative of the dipolar term is

$$-(\partial/\partial v_m)([N_A \tfrac{1}{2} f\mu^2/(1 - f\alpha)]) = -[N_A \mu^2/2(1 - f\alpha)^2](\partial f/\partial v_m). \tag{38}$$

f can be written in the form

$$f = (4\pi/3)[(2\epsilon - 2)/(2\epsilon + 1)](1/v_m) = f_1(\epsilon)/v_m. \tag{39}$$

Hence,

$$\frac{\partial f}{\partial v_m} = -\frac{f_1(\epsilon)}{v_m^2} + \frac{1}{v_m}\frac{\partial f_1(\epsilon)}{\partial v_m} \approx -\frac{f_1(\epsilon)}{v_m^2} = -\frac{f}{v_m}, \tag{40}$$

in which the neglected term $(1/v_m)[\partial f_1(\epsilon)/\partial v_m]$ is about two orders of magnitude smaller than the first term, provided that $\epsilon \gtrsim 10$, which can be assumed for a polar liquid. In view of the relation

$$\partial\beta/\partial v_m = -\beta/v_m, \tag{41}$$

we finally obtain

$$v_m \frac{\partial F_{\text{att}}}{\partial v_m} = N_A\left[\frac{1}{2}\frac{f\mu^2}{(1 - f\alpha)^2} + \frac{3}{4} f\alpha kT + 3kT\sum_{n=1}^{\infty}\frac{2\beta^2(i\xi_n) + \beta^2(i\xi_n)}{(1 + \beta(i\xi_n))^2}\right]. \tag{42}$$

The term $-vRT(\partial \log V_F/\partial v)$ was equated to $-RT$. If V_F is interpreted according to Eq. 32 the term $-RT$ should be replaced by $-RT[v_m/(v_m - v_{\text{core}})]$, but at this stage we have not attempted to refine this calculation, thus implicitly assuming $v_m \gg v_{\text{core}}$. In view of the orders of magnitude of the terms RT and $v_m(\partial F_{\text{att}}/\partial v_m)$, even a complete neglect of the term RT would not result in a serious error. For instance, at $T = 300°$ K, $RT = 0.6$ Kcal/mole, whereas $v_m(\partial F_{\text{att}}/\partial v_m)$ is about 14 Kcal/mol for carbon disulfide and 19 Kcal/mol for water.