A Model for the Surface of a Molten Salt

Jerry Goodisman
Syracuse University

R. W. Pastor
Syracuse University

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J. Goodisman* and R. W. Pastor

Department of Chemistry, Syracuse University, Syracuse, New York 13214 (Received January 16, 1978; Revised Manuscript Received May 18, 1978)

A model is proposed for the two-particle distribution functions for the surface region of a system composed of two oppositely charged species with identical hard sphere repulsions. The distribution functions are formed from those for the bulk fluid by incorporating a cutoff corresponding to the surface and a multiplying factor defined so as to guarantee electroneutrality while maintaining the proper symmetry. Various methods for doing this are discussed. Good agreement is obtained for surface tension and surface energy. Density oscillations are predicted.

I. Introduction

We consider a system composed of two oppositely charged species, with the interaction potential between a particle of species i and one of species j given by a Coulombic potential, $e_i e_j / r_{ij}$, plus a hard sphere repulsion, the hard sphere radii being identical for positively and negatively charged species (restricted primitive model).[1] This set of assumptions seems to give a good description of molten salts and other ionic systems.[2] By a model for the surface region, we mean a formula for the two-particle distribution functions $\rho_{ij}^{(2)}(\vec{r}_1\vec{r}_2)$, where[3] $\rho_{ij}^{(2)}(\vec{r}_1\vec{r}_2) \, d^3r_1 \, d^3r_2$ gives the average number of pairs of particles of species i and j, such that a particle of species i is found in a volume d^3r_1 at $\vec{r}_1$ and a particle of species j in a volume d^3r_2 at $\vec{r}_2$. From $\rho_{ij}^{(2)}(\vec{r}_1\vec{r}_2)$ one can obtain $\nabla_1\rho_i^{(1)}(\vec{r}_1)$, where $\rho_i^{(1)}$ is the one-particle distribution function or density for species i, by the Born–Yvon–Green equation.[4]

To describe a surface region, the Fowler–Kirkwood–Buff or superposition approximation[5] is often used. This approximation makes $\rho_{ij}^{(2)}(\vec{r}_1\vec{r}_2)$ identical with the corresponding distribution function of the bulk fluid as long as $\vec{r}_1$ and $\vec{r}_2$ are both within the liquid region, and zero if either is outside:

$$\rho_{ij}^{(2)}(\vec{r}_1\vec{r}_2) = \rho_{ij}^{\text{bulk}}(\vec{r}_1\vec{r}_2)[1 - \theta(z_1)][1 - \theta(z_2)] \quad (1)$$

Here z gives position on the direction normal to the surface, and $\theta(z_1)$ is the step function, equal to 1 for $z_1 > 0$ and 0 for $z_1 \leq 0$. The bulk distribution function depends only on r_{12}, reflecting the isotropy and homogeneity of the fluid. For the surface region, $\rho_{ij}^{(2)}$ may depend on z_1 and the components of $\vec{r}_{12}$. Conventionally, one includes in the Fowler approximation a step-function formula for the one-particle distribution functions. However, the assumption for $\rho^{(1)}$ is inconsistent with that for $\rho^{(2)}$, as appears[6,7] from the large and nonconstant normal pressure calculated using both assumptions. If $\rho^{(1)}$ is derived from $\rho^{(2)}$ using the Born–Yvon–Green equation, the calculated normal pressure is constant, as it should be.[6-8]

From the $\rho_{ij}^{(2)}$ one can calculate the surface tension γ and surface energy E_s. When the generalized mean spherical approximation is used to obtain ρ_{ij}^{bulk}, the results for γ and E_s for NaCl at 1128 K (see Table I) are so far from the experimental values[7] as to indicate a serious problem with the approximation (1) for $\rho_{ij}^{(2)}$, a problem which apparently is not present for one-component systems for which this model has been used. Use of a better interaction potential and ρ_{ij}^{bulk} from Monte Carlo calculations does not improve the situation.[7] The main source

TABLE I: Calculated Surface Properties of NaCl (T = 1128 K)

source	surface tension γ, dyn/cm	surface energy E^S, dyn/cm
Fowler model (superposition)	−79.58	907.52
previous model (eq 6)	42.37	111.87
present model (eq 9)	99.36	288.08
experimental	111.3ᵃ	216.2ᵇ

a G. Janz, "Molten Salts Handbook", Academic Press, New York, N.Y., 1967. *b* Calculated from $E^S = \gamma - T \, d\gamma/dt$ using values of $d\gamma/dt$ from ref a.

of the difficulty seems to lie in the violation of the electroneutrality condition.

This is best expressed by writing

$$\rho_{ij}^{\text{bulk}} = \rho_i^{\text{bulk}}\rho_j^{\text{bulk}}g_{ij}(r_{12}) \quad (2)$$

where ρ_i^{bulk} ($= \rho_j^{\text{bulk}}$) is the one-particle density of species i and defining

$$g^S(r_{12}) = \tfrac{1}{2}(g_{+-} + g_{++}) \quad (3a)$$

$$g^D(r_{12}) = \tfrac{1}{2}(g_{+-} - g_{++}) \quad (3b)$$

Of course, $g_{+-} = g_{-+}$ and $g_{++} = g_{--}$ in this model. With the assumptions of our model (eq 1) the total charge around a positive ion at $\vec{r}_1 (z_1 < 0)$ is

$$(\rho/2)^{-1} \int d\tau_2 \, e(\rho_{++}^{(2)}(\vec{r}_1\vec{r}_2) - \rho_{+-}^{(2)}(\vec{r}_1,\vec{r}_2)) =$$
$$-\rho e \int^{(z_2<0)} d\tau_2 \, g^D(r_{12}) \quad (4)$$

where $\rho = \rho_+^{\text{bulk}} + \rho_-^{\text{bulk}}$. It should equal $-e$, but, working out the integral in detail, we find[7]

$$(\rho/2)^{-1} \int d\tau_2 \, e(\rho_{++}^{(2)} - \rho_{+-}^{(2)}) =$$
$$-4\pi\rho e\left[\int_0^\infty r^2 \, dr \, g^D(r) + \tfrac{1}{2}\int_{|z_1|}^\infty r^2 \, dr \, g^D(r)(-1 + |z_1|r^{-1})\right] \quad (5)$$

Since the bulk correlation function satisfies $\int_0^\infty g^D r^2 \, dr = 1/(4\pi\rho)$, we have electroneutrality when $|z_1|$ is large, but not otherwise. The right side of (5) is plotted as a function of z_1 in Figure 1A. Henceforth, we shall represent the combination of correlation functions given in (3b) by g^B when the functions g_{+-} and g_{++} are taken from bulk calculations without modification, and use g^D for the
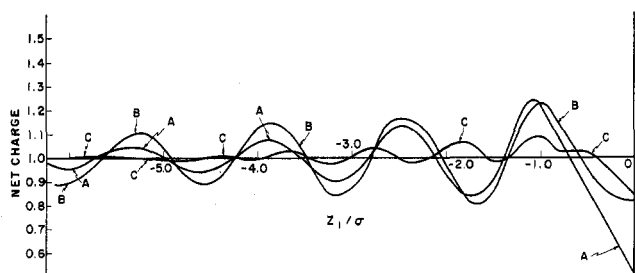
Figure 1. Electroneutrality for various models of g^D; net charge around a positive ion at z_1, in units of $-e$: curve A, unmodified Fowler model; curve B, using eq 8 for g^D; curve C, using eq 10 with f calculated according to eq 7.

corresponding function for the surface; g^D depends on z_1, z_2, and $\vec{r}_{12}$.

In our previous work, we corrected the problem by writing[7]

$$g^D = f(z_1)\, g^B(r_{12}) \tag{6}$$

where

$$f(z_1) = (4\pi\rho)^{-1}\Bigg[\int_0^\infty r^2\, dr\, g^B(r) + $$
$$\frac{1}{2}\int_{|z_1|}^\infty r^2\, dr\, g^B(r)(-1 + |z_1| r^{-1})\Bigg]^{-1} \tag{7}$$

and leaving g^S unchanged. This makes (5) exactly equal to $-e$. Much improved values for surface tension and surface energy were obtained (see Table I). We pointed out, however, that a symmetry condition was violated. We should have

$$g^D(z_1 z_2 s_{12}) = g^D(z_2 z_1 s_{12})$$

where $s_{12}^2 = (x_1 - x_2)^2 + (y_1 - y_2)^2$, and this does not hold if g^D of eq 6 is used. The present paper is concerned with correcting for electroneutrality while maintaining this symmetry.

II. A Model Satisfying the Symmetry Condition

One reasonable way of obtaining a symmetrical g from the above choice is to write

$$g^D(z_1 z_2 s_{12}) = [f(z_1)\, f(z_2)]^{1/2}\, g^B(r_{12}) \tag{8}$$

using eq 7 for f. The resultant g^D is better than g^B in assuring electroneutrality for small z_1, as shown in Figure 1B. However, it is not an improvement elsewhere. Another method was suggested by us: one could put $g^D = f(z_1)\, f(z_2)\, g^B(r_{12})$ and determine f by solving the integral equation (see eq 4)

$$\rho^{-1} = f(z_1) \int^{(z_2 < 0)} d\tau_2\, f(z_2)\, g^B(r_{12})$$

by an iterative method. Putting $f_0(z_2) = 1$, this gives for $f_1(z_1)$, the first approximation for $f(z_1)$, just eq 7. Attempts to implement this procedure were unsuccessful: we were unable to get convergence to a reasonable $f(z)$. Another solution to the symmetrization problem is to put $g^D = [f(z_1) + f(z_2)]\, g^B(r_{12})$, leading to

$$\rho^{-1} = f(z_1) \int^{(z_2 < 0)} d\tau_2\, g^B(r_{12}) + \int^{(z_2 < 0)} d\tau_2\, f(z_2)\, g^B(r_{12}) \tag{9}$$

In this case, the integral equation is linear, but the iterative procedure again failed to converge.

If it is assumed that $f(z) = 1/2$ (the asymptotic value) for $z < z_0$, eq 9 becomes a Fredholm's equation of the second kind, for which an exact method of solution is known.[9] We solved this equation for several choices of z_0
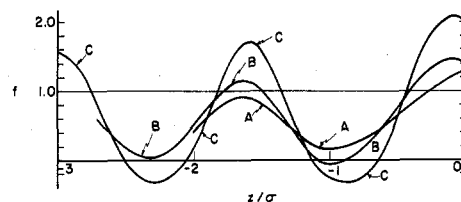

Figure 2. Solutions to the integral equation (9) for various choices of the parameter z_0 ($f(z) = 1/2$ for $z < z_0$). Curves A, B, and C correspond to $z_0 = 2.0$, 2.7, and 3.0 hard sphere diameters, respectively.

(see Figure 2). It appears that, as z_0 increases, f becomes more wildly oscillating, taking on larger positive and negative values. This probably explains our difficulties in getting solutions to the other integral equations by our iterative method.

After additional experimentation, we were led to try the physically reasonable assumption

$$g^D(z_1 z_2 s_{12}) = f(u)\, g^B(r_{12}) \qquad u = \frac{1}{2}(z_1 + z_2) \tag{10}$$

This makes the multiplying factor on g^B depend on the average of the z values of the two particles. We tried to use for f the function determined for the unsymmetrical model, according to eq 7, which uses the bulk correlation function $g^B(r) = \frac{1}{2}(g_{+-} - g_{++})$. Thus the same *function* was used as previously, but its argument was changed from z_1 to $\frac{1}{2}(z_1 + z_2)$. As shown in Figure 1C, this choice of z leads to satisfactory charge neutrality (except when z_1 is close to 0). It should be possible in principle to determine f so that electroneutrality obtained exactly when g^D of (10) was employed, but we did not pursue this route. Instead we used the f of (7) to calculate properties of the surface, as we now discuss, with satisfactory results.

III. Calculated Properties

For the purpose of these calculations, we wrote g^D in the following form:

$$g^D(z_1, z_2, s_{12}) = g^B(r_{12}) + [f(\tfrac{1}{2}z_1 + \tfrac{1}{2}z_2) - 1]g^B(r_{12})$$

This allows us to write the value for each property as the Fowler (superposition) value plus a correction. (Note that the correction is to the contribution of the electrostatic forces.) The function f (see eq 7) oscillates about unity as a function of its argument, the oscillations decreasing as the magnitude of its argument (which is always ≤ 0) increases. In fact, f is the reciprocal of the quantity plotted in Figure 1A. Calculated values of f are given in Table II (see paragraph at end of text regarding supplementary material). For $z < -7.2\sigma$, we take $f(z) = 1$, so that the correction to the Fowler value of a property (superscript F) is an integral whose range is finite. Thus, the surface tension is written

$$\gamma = \gamma^F + 2e^2 \int_{-\infty}^0 dz_1 \left(\frac{\rho}{2}\right) \int^{(z_2 < 0)} d\tau_{12} \left(\frac{\rho}{2}\right) \times$$
$$\left[\frac{x_{12}^2 - z_{12}^2}{r_{12}^3}\right]\left[f\left(\frac{z_1 + z_2}{2}\right) - 1\right]g^B(r_{12}) =$$
$$\gamma^F + \frac{e^2 \rho^2}{2} \int_{-\infty}^0 dz_1 \int_\zeta^0 dz_2 \int_0^\infty s_{12}\, ds_{12} \int_0^{2\pi} d\phi \times$$
$$\left[\frac{s_{12}^2 \cos^2\phi - z_{12}^2}{r_{12}^3}\right]\left[f\left(\frac{z_1 + z_2}{2}\right) - 1\right]g^B(r_{12}) \tag{11}$$

where $\zeta = 14.4\sigma - z_1$, $r_{12}^2 = z_{12}^2 + s_{12}^2$, and $z_{12} = -z_{21} = z_2 - z_1$; cylindrical coordinates (z_2, s_{12}, ϕ) have been used in the integral and σ is the hard sphere diameter.

As we have noted, our model of the interface is a model for the two-particle distribution functions $\rho_{++}^{(2)}$ ($= \rho_{--}^{(2)}$) and $\rho_{+-}^{(2)}$ ($= \rho_{-+}^{(2)}$), or, alternatively, their sum and difference ρ^S and ρ^D (see eq 2 and 3). We use the bulk-fluid distribution function for ρ^S, as in eq 1, and modify the bulk-fluid function for ρ^D. The one-particle distribution functions $\rho_i^{(1)}$ are to be computed from the $\rho_{ij}^{(2)}$ by the Born–Green–Yvon equation:

$$\frac{d\rho_i^{(1)}}{dz_1} = \frac{1}{kT}\sum_j \int d\tau_{12}\, u_{ij}'(r_{12})\frac{z_{12}}{r_{12}}\rho_{ij}^{(2)}(\vec{r}_{12},z_1) \quad (12)$$

Integrating (12) over all values of z_1 and noting that $\rho_{ij}^{(2)} = 0$ for $z_1 > 0$, we obtain the difference between $\rho_i(0)$ and $\rho_i(-\infty)$, which should be just the negative of the density of the anion or cation in the bulk fluid. As shown in our previous work,[7] use of the Fowler approximation (eq 1) gives the correct value, $\rho/2$, for this quantity, but, when we modify the distribution functions by multiplying ρ^B by $f(z_1)$, this no longer holds true.

This deficiency in the previous model is remedied when the modification (9), which restores the symmetry of ρ^D, is used. The effect of the correction is to add the following term to the integral of $d\rho_i^{(1)}/dz_1$:

$$\frac{1}{kT}\int_{-L}^0 dz_1 \int_{-\infty}^0 dz_2 \int_0^\infty s_{12}\, ds_{12} \times$$
$$\int_0^{2\pi} d\phi \frac{e^2}{r_{12}^2}\frac{z_{12}}{r_{12}}(-\rho_{++}^{(2)} + \rho_{+-}^{(2)}) =$$
$$\frac{4\pi e^2}{kT}\int_{-L}^0 dz_1 \int_{-\infty}^0 dz_2 \int_0^\infty s_{12}\, ds_{12}\frac{z_{12}}{r_{12}^3}[f(u) - 1]g^B(r_{12})\left(\frac{\rho}{2}\right)^2 \quad (13)$$

The value of L will eventually be allowed to become infinite; $u = \frac{1}{2}(z_1 + z_2)$. Now let $x = z_2 - z_1 = z_{12}$, and write

$$\int_0^\infty s_{12}\, ds_{12}\, r_{12}^n g^B(r_{12}) = \int_{|x|}^\infty r_{12}\, dr_{12}\, r_{12}^n g^B(r_{12}) = G^{(n+1)}(|x|) \quad (14)$$

where $G^{(i)}(y)$ is the ith moment of g^B from y to ∞, which we have previously tabulated. Equation 13 becomes

$$\frac{\pi e^2\rho^2}{kT}\int_{-L}^0 dz_1 \int_{-\infty}^0 dz_2\, x[f(u) - 1]G^{(-2)}(|x|) =$$
$$\frac{\pi e^2\rho^2}{kT}\left[\int_{-L}^0 du\, [f(u) - 1]\int_{-2u}^{2u} dx\, xG^{(-2)}(|x|) + \int_{-\infty}^{-L} du\, [f(u) - 1]\int_{(x/2)-L}^{2u} dx\, xG^{(-2)}(|x|)\right]$$

In the first term, the integral over x vanishes because the integrand is odd; if L is large enough (>7.2 hard sphere diameters in the present case) so that $f(u) = 1$ for $u < -L$, the second term also vanishes.

For calculation of $d\rho_i^{(1)}/dz_1$ at a particular value of z_1, the contribution additional to the Fowler contribution is obtained according to (see eq 13 and 14):

$$\frac{d\rho_i^{(1)}}{dz_1} = \frac{\pi e^2\rho^2}{kT}\int_{-\infty}^{-z_1} dx\, x[f(u) - 1]G^{(-2)}(|x|) =$$
$$\frac{\pi e^2\rho^2}{kT}\int_{z_0}^{-z_1} dx\, x[f(z_1 + \frac{1}{2}x) - 1]G^{(-2)}(|x|) \quad (15)$$

Here, $z_0 = -14.4\sigma - 2z_1$. The results of this calculation are given in Figure 3. The density gradient $d\rho^{(1)}/dz_1$ from the unmodified Fowler–Kirkwood–Buff model is plotted as well as $d\rho^{(1)}/dz_1$ from our model (Fowler–Kirkwood–Buff results plus correction of eq 15). It is clear that our modification leads to more pronounced oscillations, ex-
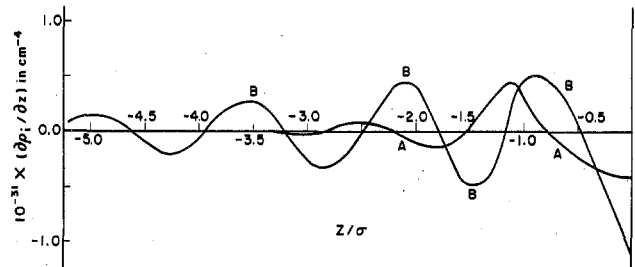

Figure 3. Gradient of the one-particle density, calculated from the two-particle distributions via the Born–Green–Yvon equation: curve A, unmodified Fowler model; curve B, present model.

tending further into the bulk. With the step function of $\rho_{ij}^{(2)}$ (eq 1), $d\rho/dz_1$ vanishes for $z_1 > 0$, while Figure 3 shows that it has its largest magnitude for z_1 just below zero. The discontinuity in $d\rho/dz_1$ could be removed by using a smooth function instead of $1 - \theta(z_1)$ in eq 1.

From $d\rho_i^{(1)}/dz_1$, one could compute the density profile, integrating inward from $z_1 = 0$. Clearly, our model predicts a density profile which has strong oscillations ($\rho_i^{(1)}(-\infty)$ is about 10^{22} cm^{-3}). This may imply that such oscillations really exist in this system: they do not seem to[8] in other surface systems studied. The enhanced oscillations represent the influence of the electroneutrality constraint, which is a reflection of the long-range character of the Coulombic force, not present in systems considered in the past. In this system, we find, furthermore, attractive forces and repulsive forces of the same range. This would seem to create the possibility that $d\rho_i^{(1)}/dz_1$ take both positive and negative values in the surface region.

Returning to the surface tension, we find, by treating (11) like (13), the following additional contribution:

$$\gamma - \gamma^F = \frac{\pi e_2\rho^2}{2}\int_{-\infty}^0 dz_1 \int_{-\infty}^0 dz_2\, [f(u) - 1] \times$$
$$\int_{|z_{12}|}^\infty r_{12}\, dr_{12}\, g^D\left(\frac{r_{12}^2 - 3z_{12}^2}{r_{12}^3}\right) =$$
$$\frac{\pi e^2\rho^2}{2}\int_{-\infty}^0 dz_1 \int_{\alpha}^{-z_1} dz_{12}\left[f\left(z_1 + \frac{z_{12}}{2}\right) - 1\right][G^{(0)}(|z_{12}|) - 3z_{12}^2 G^{(-2)}(|z_{12}|)] \quad (16)$$

For the surface energy, we find

$$E^S - E^{S,F} = \frac{1}{2}\int_{-\infty}^0 dz_1 \int d\tau_{12}\sum_{ij} u_{ij}(r_{12})[\rho_{ij}^{(2)}(\vec{r}_{12},z_1) - \rho_{ij}^{(2)}(r_{12},z_1)^{FKB}] = (\rho/2)^2\int_{-\infty}^0 dz_1 \int_{-\infty}^0 dz_2 \int_0^\infty ds_{12}\, s_{12} \times$$
$$\int_0^{2\pi} d\phi(e^2/r_{12})(-2g^B)[f(u) - 1] =$$
$$-e^2\pi\rho^2\int_{-\infty}^0 dz_1 \int_{\alpha}^{-z_1} dz_{12}[f(z_1 + \frac{1}{2}z_{12}) - 1]G^{(0)}(|z_{12}|) \quad (17)$$

with $u = \frac{1}{2}(z_1 + z_2)$, $\alpha = 2(-7.2\sigma - z_1)$, and $G^{(0)}$ defined by (14). Since the moments of g^B have been previously calculated, a double integral over z_1 and z_{12} is required to evaluate the additional contributions to γ and to E^S. They are 178.94 and -619.44 dyn/cm, respectively. As shown in Table I, the total values for surface tension and surface energy are in reasonable agreement with experiment. As usual, the agreement is much better for the former.

We conclude that satisfaction of the electroneutrality and symmetry conditions on the two-particle distribution functions converts the Fowler–Kirkwood–Buff model of the surface region, untenable for this system, into one which could provide a reasonable description of the interface. What one requires now are additional constraints

enabling us to further refine the model (only g^D, and not g^S (eq 3 and 4) has been altered), or further data for testing the predictions of the model. In particular, there is the fact that the improvement in calculated properties between the Fowler–Kirkwood–Buff and the present model is accompanied by a large increase in the oscillations in the one-particle distribution function or density.

One thermodynamic property which should be satisfied by the statistical mechanical model for the interface is the Gibbs–Helmholtz equation

$$E^S = \gamma - T(\partial \gamma / \partial T)$$

Verifying this equation is difficult; furthermore, it is likely that the sharp cutoffs in ρ_{ij} (eq 1) become worse approximations as the temperature increases. The fact that E^S agrees much less well with experiment than γ may be taken[8] as an indication that the Gibbs–Helmholtz equation is not satisfied. Another property is expressed by the Gibbs–Lippmann equation

$$(\partial \gamma / \partial E_p)_T = -q$$

where E_p is the drop in electrical potential across the interface and q the electrical charge per unit area of the surface double layer.[10] The present model of course has neither double layer nor potential drop. Modification of the assumptions, to produce asymmetries between anions and cations, would be interesting to study.

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Spectroscopy of Polyenes. 1. Comprehensive Investigation of Absorption Spectra of Polyenals and Polyenones Related to Visual Chromophores

Paritosh K. Das and Ralph S. Becker*

Department of Chemistry, University of Houston, Houston, Texas 77004 (Received March 23, 1978)

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The absorption spectra of various homologues and analogues of retinals, a total of 21, with varying number of double bonds (n) have been examined in detail under various conditions of solvent and temperature. Altogether six band systems have been identified and their oscillator strengths and transition energies are presented as functions of chain length. The origin of the transitions is discussed in the light of the results of semiempirical calculations available in the literature. The trend in the lower polyene systems ($n = 2$–4) where the $^1(n,\pi^*)$ state is seen in absorption clearly indicates that this latter state is the lowest singlet state in these systems, and is close to the B_u state in retinals and their analogues. The ~280-nm band system in retinals and their analogues, heretofore not satisfactorily assigned, is traceable to a more intense band system in the lower homologues and is tentatively interpreted in terms of absorption of 6-s-trans conformers present in solution to the extent of ~10% in equilibrium with distorted 6-s-cis conformers. The absorption spectra of retinones and C_{18} ketones indicate methyl–methyl and methyl–hydrogen steric interaction leading to geometric distortion of the polyene chain.

I. Introduction

In recent years, a great deal of theoretical and experimental work has been done on retinals and related polyene systems.[1-4] However, a number of questions and controversies regarding the spectral properties of these systems still remain unresolved. Some of these concern the relative order of the three low-lying singlet states, $^1A_g^-$, ^1B_u, and $^1(n,\pi^*)$,[5-10] the nature of the lowermost singlet state,[11-14] the location of the cis band ($^1A_g^+ \leftarrow {}^1A_g$ transition),[3,6,7,15] the assignment of the 280–300-nm band system (in retinals),[3,16b,17] and the absorption spectral behavior of the 14-methyl analogue of 11-*cis*-retinal.[18,19]

In the present investigation, we have studied 21 polyenals and polyenones that are related to retinals as analogues and homologues. The low-lying excited states

of photophysical and photochemical interest in many of these systems are expected to be comparatively sparsely located and to provide situations with relative state order different from that in retinals. Although there have been a few early spectroscopic studies[20-22] on some of the polyene systems under examination, these were concerned with room temperature spectra and limited to band maxima (as routine work in the course of synthesis). No detailed systematic analysis has ever been undertaken with the object of understanding the existent problems concerning retinals, their homologues, and visual pigments.

In paper 1, we propose to present the absorption spectral data and attempt to interpret them in the light of the results of theoretical calculations available to date. In paper 2, we shall report the data on fluorescence, quantum