Statistical Thermodynamics of Solutions of Optically Active Substances. I. Excess Free Energy of Binary Solution of d- and l-Isomers

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In recent years considerable progress has been made in the field of the theory of solutions and the fundamental features of various types of binary solutions such as polymer solutions, and associated solutions, etc. were explained theoretically. However, there seem to be no papers which treat the problem of of the solutions containing optical isomers. In this paper the idea of interaction of surface points in groups will be introduced to elucidate the fundamental features of the solution consisting of optical isomers.

The Model of the Solutions of Optical Isomers

In the statistical mechanical lattice theory of solutions of anisotropic molecules, the model usually adopted is that the surface of the molecule is devided into a definite number of contact points and each contact point is grouped into an energetically equivalent element and the number of contact points belonging to each group has a definite value. The configurational energy of the system is a sum of interaction energies of the pairs of each contact point. In such a model, however, the mutual configuration of different kinds of elements in one and the same molecule is not taken into account.

According to the above model, the molecules of *d*- and *l*-optical isomers have the same number of contact points of the same kind of elements, so that these two kinds of molecules cannot be distinguished. In order to distinguish one isomer from the other, mutual configuration of contact points of different kinds in one and the same molecule must be introduced into the above model, and at least three contact points of different kinds of elements must interact in groups at a time.

To meet the above requirement the following model is proposed.

(1) The molecule is a regular polyhedron composed of z planes of which one consists of a-element and the remaining $z-1$ ones are consist of b-elements, and further, the a-element is composed of three sub-elements 1, 2, 3, the arrangement of these three elements, viewed toward the plane from the outside of the molecule along the direction normal to it, is in the order, 1, 2, 3 clockwise for *d*-isomers and 1, 3, 2 for *l*-isomers, the mirror image of *d*-isomers.

(2) Each molecule occupies one site of the quasi-crystalline lattice of z nearest neighbors, and the molecular axis which passes the center of the molecule and the a-plane composed of a-element can take z directions. When the direction is specified, it can take 3 further different arrangements by the rotation around the axis and thus the molecule at one site can have $3z$ orientational freedom in all*.

(3) The molecules contact with plane to plane and the total configurational energy of the system is the sum of the interaction energy of pairs of planes, the kind of pair of planes is $a-a$, $a-b$ and $b-b$ and the $a-a$ pair contains 6 kinds of sub pairs, 11, 22, 33, 12, 13 and 23 and ab pair 3 kinds of sub pairs, $b1$, $b2$ and $b3$. If a-elements of *l*-isomers and *d*-isomers are denoted by a_l and a_d respectively, the a_l-a_l pair can take 3 configurations $\begin{pmatrix}1&2&3\\1&3&2\end{pmatrix}$, $\begin{pmatrix}1&2&3\\2&1&3\end{pmatrix}$ and $\begin{pmatrix}1&2&3\\3&2&1\end{pmatrix}$ with interaction energy $\omega_{11}+2\omega_{23}$, $2\omega_{12}+\omega_{33}$ and $2\omega_{13}+\omega_{22}$ respectively, where ω_{ij} denotes the interaction energy of a pair of i and j element.

For a_d-a_d pair the same value of interaction energy is obtained for each configuration. For a_l-a_d pair, three configurations are represeted $\begin{pmatrix}1&2&3\\1&2&3\end{pmatrix}$, $\begin{pmatrix}1&2&3\\3&1&2\end{pmatrix}$ and $\begin{pmatrix}1&2&3\\2&3&1\end{pmatrix}$ with interaction energy $\omega_{11}+\omega_{22}+\omega_{33}$, $\omega_{12}+\omega_{13}+\omega_{23}$ and $\omega_{12}+\omega_{13}+\omega_{23}$ respectively, can take place.

$\begin{pmatrix}1&2&3\\1&2&3\end{pmatrix}$ means the configuration in which sub elements 1, 2 and 3 of a_d plane of *d*-isomers interact with sub element of 1, 2 and 3 of a_l plane of *l*-isomers forming sub pairs 11, 22 and 33. Generally, distinguishable pairs are obtained by cycling the lower row of numbers without permutation.

The Configurational Partition Function and the Excess Free Energy

Using the above model, the configurational partition functions and the excess free energy

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* Strictly speaking the regular polyhedron must have a symmetry of C_{3n} around all of z axes passing through the center of the molecule and that of each of z planes.

of the binary system of *d*- and *l*-optical isomers were derived based on the method of expansion of Kirkwood[1].

Generally configurational partition function Ω is, by definition, expressed as

$$\Omega=\sum e^{-E/kT} \tag{1}$$

where E denotes the potential energy of a system for a particular configuration and summation is carried out over all configurations.

For the system of pure *l*-isomers, its configurational partition function Ω_l is represented

$$\begin{aligned}\Omega_l&=\sum e^{-E_l/kT}=e^{-\bar{E}_l/kT}(\sum e^{-(E_l-\bar{E}_l)/kT})\\&=e^{-\bar{E}_l/kT}(\sum e^{-W_l/kT})\end{aligned} \tag{2}$$

where E_l denotes the potential energy of the system of pure *l*-isomers and $\bar{E}_l$ denotes the unweighted average of E_l over all configurations and W_l denotes $E_l-\bar{E}_l$. If g_l denotes the number of distinguishable configurations of the system consisting of N_l molecules of *l*-isomer, then the configurational partition function of the system is expressed, following Kirkwood[1], as

$$\ln\Omega_l-\ln g_l-\frac{N_l\chi_l}{\boldsymbol{kT}}=\sum\ln\frac{1}{g_l}\sum e^{-W_l(N_l)/kT} \tag{3}$$

where $N_l\chi_l=\bar{E}_l$ and g_l according to the above model, is equal to $(3z)^{N_l}$.

By the use of an auxiliary quantity h_l defined by

$$h_l=1-\frac{1}{g_l}\sum e^{-W_l(N_l)/kT} \tag{4}$$

Eq. 3 can be rewritten as

$$\begin{aligned}&\ln\Omega_l-N_l\ln 3z-\frac{N_l\chi_l}{\boldsymbol{kT}}\ln(1-h_l)\\&=-h_l-\frac{1}{2}h_l^2-\frac{1}{3}h_l^3-\frac{1}{4}h_l^4-\cdots\cdots\end{aligned} \tag{5}$$

If the h_l in Eq. 4 is expanded in powers of $W_l(N_l)/\boldsymbol{kT}$, the following formula is obtained.

$$\begin{aligned}h_l=&\frac{\langle W_l(N_l)\rangle_{Av.}}{\boldsymbol{kT}}-\frac{\langle W_l^2(N_l)\rangle_{Av.}}{2!\ (\boldsymbol{kT})}\\&+\frac{\langle W_l^3(N_l)\rangle_{Av.}}{3!\ (\boldsymbol{kT})^3}-\cdots\cdots\end{aligned} \tag{6}$$

where $\langle W_l(N_l)\rangle_{Av.}$ denotes the unweighted average of $W_l(N_l)$ over all configurations, and similarly $\langle W_l^t(N_l)\rangle_{Av.}$ denotes the unweighted average of the t th power of $W_l(N_l)$ over all configurations. Substituting 6 into 5 the following expression is obtained.

$$\begin{aligned}\ln\Omega_l-N_l\ln 3z-\frac{N_l\chi_l}{\boldsymbol{kT}}=&-\frac{\langle W_l(N_l)\rangle_{Av.}}{\boldsymbol{kT}}\\&-\{\langle W_l(N_l)\rangle^2{}_{Av.}-\langle W_l^2(N_l)\rangle_{Av.}\}/2!\ (\boldsymbol{kT})^2\\&-\{\langle W_l^3(N_l)\rangle_{Av.}\\&-3\langle W_l(N_l)\rangle_{Av.}\langle W_l(N_l)\rangle_{Av.}\}/3!\ (\boldsymbol{kT})^3\\&-\{2\langle W_l(N_l)\rangle^3{}_{Av.}\}/3!\ (\boldsymbol{kT})^3-\cdots\cdots\end{aligned} \tag{7}$$

As $\bar{E}_l$ is the unweighted average of E_l, it follows that

$$\langle W_l(N_l)\rangle_{Av.}=\overline{(E_l-\bar{E}_l)}=\bar{E}_l-\bar{E}_l=0 \tag{8}$$

Then Eq. 7 is rewritten as

$$\begin{aligned}\ln\Omega_l-N_l\ln 3z-\frac{N_l\chi_l}{\boldsymbol{kT}}=&\frac{\langle W_l^2(N_l)\rangle_{Av.}}{2!\ (\boldsymbol{kT})^2}\\&-\frac{\langle W_l^3(N_l)\rangle_{Av.}}{3!\ (\boldsymbol{kT})^3}-\cdots\cdots\end{aligned} \tag{9}$$

Similarly, for the system of N_d *d*-isomers, the following expression is obtained.

$$\begin{aligned}\ln\Omega_d-N_d\ln 3z-\frac{N_d\chi_d}{\boldsymbol{kT}}=&\frac{\langle W_d^2(N_d)\rangle_{Av.}}{2!\ (\boldsymbol{kT})^2}\\&-\frac{\langle W_d^3(N_d)\rangle_{Av.}}{3!\ (\boldsymbol{kT})^3}-\cdots\cdots\end{aligned} \tag{10}$$

In the following, it will be shown that χ_l is equal to χ_d. As χ_l is the unweighted average of E_l over all configurations, χ_l is proportional to

$$\bar{\omega}_{a_l-a_l}+2(z-1)\bar{\omega}_{a_l-b}+(z-1)^2\bar{\omega}_{b-b} \tag{11}$$

and similarly χ_d is proportional to

$$\bar{\omega}_{a_d-a_l}+2(z-1)\bar{\omega}_{a_d-b}+(z-1)^2\cdot\bar{\omega}_{b-b} \tag{12}$$

where ‒ denotes the unweighted average and $\omega_{a_l-a_l}$, $\omega_{a_l-a_d}$, ω_{a_l-b}, ω_{a_d-b} and ω_{b-b} denote the interaction energy of a_l-a_l, a_d-a_d, a_l-b, a_d-b and $b-b$ plane pairs respectively.

Further, according to the assumption made above, the following relation is obtained.

$$\begin{aligned}\bar{\omega}_{a_l-a_l}&=\frac{1}{3}\{\omega_{11}+\omega_{22}+\omega_{33}+2(\omega_{12}+\omega_{23}+\omega_{31})\}\\&=\bar{\omega}_{a_d-a_d}\end{aligned} \tag{13}$$

Thus each of three different configurations of a_l-a_l a_d-a_d pair of plane have the same interaction energy. Further

$$\bar{\omega}_{a_l-b}=\omega_{1b}+\omega_{2b}+\omega_{3b}=\bar{\omega}_{a_d-b} \tag{14}$$

From 11, 12, 13 and 14, we obtain

$$\chi_l=\chi_d=\chi_0 \tag{15}$$

As is stated above, the interaction energy of the pairs of planes in *l*-isomers $\omega_{a_l-a_l}$, ω_{a_l-b} and ω_{b-b} and in *d*-isomers $\omega_{a_d-a_d}$, ω_{a_d-b} and ω_{b-b} have the same value, and the total energy E is the sum of such interaction energies of pairs of planes. Further for one specified configuration in the system consisting of N_0 molecules of *l*-isomers, with a specified number of pairs of a_l-a_l, a_l-b and $b-b$ plane contacts,

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[1] J. G. Kirkwood, *J. Chem. Phys.*, 6, 70 (1938).

there exists the corrsponding configuration in the system contisting of N_0 molecules of *d*-isomers, for, one to one correspondence exists between both isomers.

Then the total configurational energy for one specified configuration for *l*-isomers is equal to that of the corresponding configuration in α-isomers, that is

$$E_l = E_d \tag{16}$$

and hence

$$W_l(N_0) = W_d(N_0) = W_0(N_0) \tag{17}$$

For $d-l$ mixtures consisting of N_l *l*-isomers and N_d *d*-isomers, the configurational partition function Ω_{dl} is expressed as

$$\begin{aligned}
&\ln \Omega_{dl} - N \ln 3z - \ln \frac{N!}{(Nx)!\ \{N(1-x)\}!} \\
&- N\cdot\chi_{ld}(x)/\boldsymbol{k}T = -\langle W_{dl}(N, x)\rangle_{Av.}/\boldsymbol{k}T \\
&- \{\langle W_{dl}(N, x)\rangle^2{}_{Av.} \\
&- \langle W^2_{dl}(N, x)\rangle_{Av.}\}/2!\ (\boldsymbol{k}T)^2 \\
&- \{\langle W^3_{dl}(N, x)\rangle_{Av.} - 3\langle W^2_{dl}(N, x)\rangle_{Av.} \\
&\quad \cdot\langle W_{dl}(N, x)\rangle_{Av.}\}/3!\ (\boldsymbol{k}T)^3 \\
&- 2\langle W_{dl}(N, x)\rangle^3{}_{Av.}/3!\ (\boldsymbol{k}T)^3
\end{aligned} \tag{18}$$

where $N = N_l + N_d$ and $N\cdot\chi_{dl}(x)$ is the unweighted mean of interaction energy of the system and $x = N_l/N$. Since $\chi_{dl}(x)$ is proportional to

$$\begin{aligned}
&x^2\{\overline{\omega}_{a_l-a_l} + 2(z-1)\overline{\omega}_{a_l-b} + (z-1)^2\omega_{b-b}\} \\
&\quad + 2(1-x)x\{\omega_{a_l-a_d} + (z-1)(\omega_{a_l-b} + \omega_{a_d-b}) \\
&\quad + (z-1)^2\omega_{b-b}\} + (1-x)^2 \\
&\quad \{\omega_{a_d-a_d} - 2(z-1)\overline{\omega}_{a_d-b} + (z-1)^2\omega_{b-b}\}
\end{aligned} \tag{19}$$

$\overline{\omega}_{a_l-a_d}$ is the mean of three interaction energies

$$\omega_{11} + \omega_{22} + \omega_{33},\ \omega_{12} + \omega_{23} + \omega_{31},\ \omega_{12} + \omega_{23} + \omega_{31}$$

Each term differs from that of $\omega_{a_l-a_l}$ or $\omega_{a_d-a_d}$ but the unweighted mean over these three configurations, becomes the same value as follows:

$$\begin{aligned}
\overline{\omega}_{a_d-a_l} &= \frac{1}{3}(\omega_{11} + \omega_{22} + \omega_{33} + \omega_{12} + \omega_{23} + \omega_{31} \\
&\qquad + \omega_{12} + \omega_{23} + \omega_{31}) \\
&= \frac{1}{3}\{\omega_{11} + \omega_{22} + \omega_{33} + 2(\omega_{12} + \omega_{23} + \omega_{31})\} \\
&= \omega_{a_l-a_l} = \omega_{a_d-a_d}
\end{aligned} \tag{20}$$

Hence, from 19, 20, 11 and 12, we have

$$\chi_{dl}(x) = \chi_l = \chi_d = \chi_0 \tag{21}$$

$$\langle W_{dl}(N, x)\rangle_{Av.} = \overline{(E_{dl} - \overline{E}_{dl})} = \overline{E}_{dl} - \overline{E}_{dl} = 0 \tag{22}$$

For the system consisting of N *d*-isomers or N *l*-isomers, free energy is expressed as

$$\begin{aligned}
F_d = F_l &= -\boldsymbol{k}T \ln \Omega_0 = N\boldsymbol{k}T \ln 3z + N\chi_0 \\
&\quad + \frac{\langle W^2_0(N)\rangle_{Av.}}{2!\ (\boldsymbol{k}T)} - \frac{\langle W^3_0(N)\rangle_{Av.}}{3!\ (\boldsymbol{k}T)^2} + \cdots\cdots
\end{aligned} \tag{23}$$

For $d-l$ mixtures consisting of $N_l(=Nx)$ molecules of *l*-isomer and $N_d\ (=N(1-x))$ molecules of *d*-isomer, we obtain

$$\begin{aligned}
F_{dl} &= -\boldsymbol{k}T \ln \Omega_{dl} = N\boldsymbol{k}T \ln 3z + N\chi_0 \\
&\quad + N\boldsymbol{k}T\{x \ln x + (1-x) \ln (1-x)\} \\
&\quad + \frac{\langle W^2_{dl}(N, x)\rangle_{Av.}}{2(\boldsymbol{k}T)} - \frac{\langle W^3_{dl}(N, x)\rangle_{Av.}}{3!\ (\boldsymbol{k}T)^2} \\
&\quad + \cdots\cdots
\end{aligned} \tag{24}$$

As each configuration has a different energy, that is $W_{dl} = (N, x) \neq W_0(N)$, then the free energy of mixing ΔF_m is represented as

$$\begin{aligned}
\Delta F_m &= N\boldsymbol{k}T\{x \ln x + (1-x) \ln (1-x)\} \\
&\quad + \frac{1}{2(\boldsymbol{k}T)}\{\langle W^2_{dl}(N, x)\rangle_{Av.} - \langle W^2_0(N_l)\rangle_{Av.} \\
&\quad - \langle W^2_0(N_d)\rangle_{Av.}\} - \frac{1}{3!\ (\boldsymbol{k}T)^2} \\
&\quad \times\{\langle W^3_{dl}(N, x)\rangle_{Av.} - \langle W^3_0(N_l)\rangle_{Av.} \\
&\quad - \langle W^3_0(N_d)\rangle_{Av.}\} + \cdots\cdots
\end{aligned} \tag{25}$$

Then the problem is reduced to a calculation of second and heigher powers of $W_{dl}(N, x)$, $W_0(N_l)$ and $W_0(N_d)$. Now $\langle W^2_0(N_l)\rangle$, $\langle W^2_0(N_d)\rangle$ and $W^2_{dl}(N)$ will be considered.

According to the model mentioned above, potential energy E of the system consisting of N molecules of *l*- or *d*-isomers with the particular configuration having N_{bb} *bb* pairs, N_{ab} *ab* pairs, N_{aa_1} aa_1 pairs, N_{aa_2} aa_2 pairs and N_{aa_3} aa_3 pairs, where aa_1, aa_2 and aa_3 denote three kinds of *aa* contact, is expressed as

$$\begin{aligned}
E &= N_{bb}\omega_{bb} + N_{ab}\omega_{ab} + N_{aa_1}\omega^0_{aa_1} + N_{aa_2}\omega^0_{aa_2} \\
&\quad + N_{aa_3}\omega^0_{aa_3}
\end{aligned} \tag{26}$$

where $\omega^0_{aa_1}$, $\omega^0_{aa_2}$ and $\omega^0_{aa_3}$ denote those interaction energies corresponding to aa_1, aa_2 and aa_3 pairs respectively and these values are $\omega_{11} + 2\omega_{23}$, $\omega_{22} + 2\omega_{13}$ and $\omega_{33} + 2\omega_{12}$ respectively. Then the average value E becomes

$$\begin{aligned}
E &= \overline{N}_{bb}\omega_{bb} + \overline{N}_{ab}\omega_{ab} + \overline{N}_{aa_1}\omega_{aa_1} \\
&\quad + \overline{N}_{aa_2}\omega_{aa_2} + \overline{N}_{aa_3}\omega_{aa_3} \\
&= \frac{1}{2}zN\left\{\frac{(z-1)^2}{z^2}\omega_{bb} + \frac{2(z-1)}{z^2}\omega_{ab}\right. \\
&\quad \left. + \frac{1}{z^2}\cdot\frac{1}{3}(\omega_{aa_1} + \omega_{aa_2} + \omega_{aa_3})\right\}
\end{aligned} \tag{27}$$

As $W_0(N)$ means the difference between the potential energy of the system of particular configuration and that averaged over all configurations, $W_0(N)$ for the particular configuration mentioned above becomes

$$W_0(N)=E-\bar{E}=\left\{N_{bb}-\frac{1}{2}N\frac{(z-1)^2}{z}\right\}\omega_{bb}$$
$$+\left\{N_{ab}-\frac{N(z-1)}{z}\right\}\omega_{ab}$$
$$+N_{aa_1}\omega^0_{aa_1}+N_{aa_2}\omega^0_{aa_2}+N_{aa_3}\omega^0_{aa_3}$$
$$-\frac{1}{6}\frac{N}{z}(\omega^0_{aa_1}+\omega^0_{aa_2}+\omega^0_{aa_3}) \qquad (28)$$

In calculating $\langle W_0^2(N)\rangle_{Av.}$, we must strictly take the average over all possible configurations. However, since of all configurations the configurations with $N_{bb}=\bar{N}_{bb}$, $N_{ab}=\bar{N}_{ab}$ and $\sum_{i=1}^{3}{}_{aa_i}=\bar{N}_{aa}$ occupy the predominant part, and the average over these configurations, may differ very little from that over all configurations, we approximately take the former average in place of the latter. Then

$$W_0(N)=\sum_{i=1}^{3}{}'N_{aa_i}\omega^0_{aa_i}-\frac{1}{6}\frac{N}{z}(\sum_{i=1}^{3}\omega^0_{aa_i}) \qquad (29)$$

where $\sum'$ donates the summation under the restriction that $\sum_{i=1}^{3}N_{aa_i}=1/2\cdot N/z$ and $\langle W_0^2(N)\rangle_{Av}$. becomes

$$\langle W_0^2(N)\rangle=\overline{(\sum_{i=1}^{3}{}'N_{aa_i}\omega^0_{aa_i})^2}-2\sum_{i=1}^{3}{}'N_{aa_i}\omega^0_{aa_i}$$
$$\times\frac{1}{6}\frac{N}{Z}(\sum_{i=1}^{3}\omega^0_{aa_i})+\left(\frac{1}{6}\frac{N}{z}\sum_{i=1}^{3}\omega^0_{aa_i}\right)^2$$
$$=(\sum_{i=1}^{3}{}'N_{aa_i}\omega^0_{aa_i})^2-\left(\frac{1}{6}\frac{N}{z}\sum_{i=1}^{3}\omega^0_{aa_i}\right)^2 \qquad (30)$$

As all configurations of *aa* pair can take place with equal probability the first term of 30 becomes

$$(\sum_{i=1}^{3}{}'N_{aa_i}\omega^0_{aa_i})^2=\left(\frac{1}{2}\frac{N}{z}\right)^2\int_0^1\int_0^y[\{\omega^0_{aa_1}x$$
$$+\omega^0_{aa_2}(y-x)\}+\omega^0_{aa_3}(1-y)]^2\mathrm{d}x\mathrm{d}y$$
$$=\left(\frac{1}{2}\frac{N}{z}\right)^2\frac{1}{6}(\omega^{0\,2}_{aa_1}+\omega^{0\,2}_{aa_2}+\omega^{0\,2}_{aa_3}$$
$$+\omega^0_{aa_1}\omega^0_{aa_2}+\omega^0_{aa_2}\omega^0_{aa_1}+\omega^0_{aa}\omega_3{}^0_{aa_1}) \qquad (31)$$

Substituting 31 into 30 the following formula is obtained:

$$\langle W_0^2(N)\rangle_{Av}=\left(\frac{1}{2}\frac{N}{z}\right)^2\cdot\frac{1}{36}\{(\omega^0_{aa_1}-\omega^0_{aa_2})^2$$
$$+(\omega^0_{aa_2}-\omega^0_{aa_3})^2+(\omega^0_{aa_3}-\omega^0_{aa_1})^2\} \qquad (32)$$

For the system consisting of N_l molecules of *l*-isomers and N_d molecules of *d*-isomer, $\langle W_{dl}^2(Nx)\rangle$, where $N=N_l+N_d$ and $x=N_l/(N_l+N_d)$, can be obtained in a similar way. In this case the average may be taken over the configurations in which $N^{ll}_{aa}=\overline{N^{ll}_{aa}}=Nx^2/2z$, $N^{dl}_{aa}=\overline{N^{dl}_{aa}}=Nx(1-x)/z$ and $N^{dd}_{aa}=\overline{N^{ll}_{aa}}=N(1-x)^2/2z$ where N^{ll}_{aa}, N^{dl}_{aa} and N^{dd}_{aa} are the number of pairs of a_l-a_l, a_l-a_d and a_d-a_d respectively. The a_l-a_d pair can have three different configuration with corresponding interaction energies $\omega^{ld}_{aa_1}$, $\omega^{ld}_{aa_2}$ and $\omega^{ld}_{aa_3}$. As mentioned above $\omega^{ld}_{aa_1}=\omega_{11}+\omega_{22}+\omega_{33}$, $\omega^{ld}_{aa_2}=\omega^{ld}_{aa_3}=\omega_{12}+\omega_{13}+\omega_{23}$, then

$$\sum_{i=1}^{3}\omega^{ld}_{aa_i}=\omega_{11}+\omega_{22}+\omega_{33}+2(\omega_{12}+\omega_{13}+\omega_{23})$$
$$=\sum_{i=1}^{3}\omega^{ll}_{aa_i}=\sum_{i=1}^{3}\omega^{dd}_{aa_i}=\sum_{i=1}^{3}\omega^0_{aa_i} \qquad (33)$$

From 33 the following expressions are obtained.

$$W_{dl}(N,x)=\sum_{i=1}^{3}{}'(N^{ll}_{aa_i}\omega^{ll}_{aa_i}+N^{ld}_{aa_i}\omega^{ld}_{aa_i}$$
$$+N^{dd}_{aa_i}\omega^{dd}_{aa_i})-\frac{1}{6}\frac{N}{z}(\sum_{i=1}^{3}\omega^0_{aa_i})$$
$$=\sum_{i=1}^{3}{}'\left\{N^{ll}_{aa_i}\omega^{ll}_{aa_i}-\frac{Nx^2}{2z}\left(\frac{1}{3}\sum_{i=1}^{3}\omega^{ll}_{aa_i}\right)\right\}$$
$$+\sum_{i=1}^{3}{}'\left\{N^{ld}_{aa_i}\omega^{ld}_{aa_i}-\frac{Nx(x-1)}{z}\left(\frac{1}{3}\sum_{i=1}^{3}\omega^{dl}_{aa_i}\right)\right\}$$
$$+\sum_{i=1}^{3}{}'\left\{N^{dd}_{aa_i}\omega^{dd}_{aa_i}-\frac{N(1-x)^2}{2z}\left(\frac{1}{3}\sum_{i=1}^{3}\omega^{dd}_{aa_i}\right)\right\} \qquad (34)$$

where $\sum'$ denotes the summation under the restrictions that $\sum_{i=1}^{3}N^{ll}_{aa_i}=Nx^2/2Z$, $\sum_{i=1}^{3}N^{dl}_{aa_i}=Nx(1-x)/z$ and $\sum_{i=1}^{3}N^{dd}_{aa_i}=(1-x)^2/2z$. Since the mean values in { } of 34 become zero, then

$$\langle W_{dl}^2(N,x)\rangle_{Av}=\left(\frac{1}{2}\frac{N}{z}x^2\right)^2\cdot\frac{1}{36}\{(\omega^{ll}_{aa_1}-\omega^{ll}_{aa_2})^2$$
$$+(\omega^{ll}_{aa_2}-\omega^{ll}_{aa_3})^2+(\omega^{ll}_{aa_3}-\omega^{ll}_{aa_1})^2\}$$
$$+\left\{\frac{Nx(1-x)}{z}\right\}^2\cdot\frac{1}{36}\{(\omega^{dl}_{aa_1}-\omega^{dl}_{aa_2})^2$$
$$+(\omega^{dl}_{aa_2}-\omega^{dl}_{aa_3})^2+(\omega^{dl}_{aa_3}-\omega^{dl}_{aa_1})^2\}$$
$$+\left\{\frac{1}{2}\frac{N}{z}(1-x)^2\right\}^2\cdot\frac{1}{36}\{(\omega^{dd}_{aa_1}-\omega^{dd}_{aa_2})^2$$
$$+(\omega^{dd}_{aa_2}-\omega^{dd}_{aa_3})^2+(\omega^{dd}_{aa_3}-\omega^{dd}_{aa_1})^2\}$$
$$=\left(\frac{1}{2}\frac{N}{z}\right)^2\{x^4+(1-x)^4\}\cdot\frac{1}{36}$$
$$\times\{(\omega^0_{aa_1}-\omega^0_{aa_2})^2+(\omega^0_{aa_2}-\omega^0_{aa_3})^2$$
$$+(\omega^0_{aa_3}-\omega^0_{aa_1})^2\}+\left(\frac{N}{z}\right)x^2(1-x)^2$$
$$\times\frac{1}{36}\{(\omega^{dl}_{aa_1}-\omega^{dl}_{aa_2})^2+(\omega^{dl}_{aa_2}-\omega^{dl}_{aa_3})^2$$
$$+(\omega^{dl}_{aa_3}-\omega^{dl}_{aa_1})^2\} \qquad (35)$$

If the terms higher than second power of W in 25 are neglected, free energy of mixing $\Delta_m F$ or excess free energy F^E may be expressed as

$$
\begin{aligned}
&\Delta_m F - NkT\{x \ln x + (1-x) \ln (1-x)\} = F^E \\
&= -\frac{1}{2kT}\left[\left(\frac{1}{2}\ \frac{N}{z}\right)^2 \{x^4 + (1-x)^4 \right. \\
&\quad - x^2 - (1-x)^2\} \times \frac{1}{36}\{(\omega^0_{a a_1} - \omega^0_{a a_2})^2 \\
&\quad + (\omega^0_{a a_2} - \omega^0_{a a_3})^2 + (\omega^0_{a a_3} - \omega^0_{a a_1})\} \\
&\quad + \left(\frac{N}{z}\right)^2 x^2 (1-x)^2 \times \frac{1}{36}\{(\omega^{dl}_{a a_1} - \omega^{dl}_{a a_2})^2 \\
&\quad + (\omega^{dl}_{a a_2} - \omega^{dl}_{a a_3})^2 + (\omega^{dl}_{a a_3} - \omega^{dl}_{a a_1})^2\} \qquad (36)
\end{aligned}
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Discussions

As is seen from the above result the principal term of excess free energy F^E is inversely proportional to absolute temperature. This is due to the fact that the optical *d*- and *l*-isomers are energetically identical in random mixture (see Eqs. 21 and 22), so that the first order terms are dropped in the expansion. It is in remarkable contrast to that of the usual binary solutions where the principal terms of F^E are independent of temperature.

Dependency of the term on mole fraction x of one component is complicated and is higher than quadratic in x. This is another feature of the system of optically active substances.

The term is usually very small and is quite negligible.

However, if the difference $|\omega^0_{a a_i} - \omega^0_{a a_j}|$ or $|\omega^{dl}_{a a_i} - \omega^{dl}_{a a_j}|$ happens to be great, the contribution from these terms may become appreciable. For instance consider an optical active molecule whose sub elements 1, 2 and 3 are $-NH_2$, $-C{=}O$ and $-OH$ group respectively. Then hydrogen bonding is formed between the pairs 1−2, 1−3, 2−3 and 3−3 but is not formed between pairs 1−1 and 2−2.

If we assume that interaction energies of these pairs which form hydrogen bonding are all equal and 5 kcal./mol. and those of the pairs which do not form hydrogen bonding are neglected, then F^E becomes according to 36.

$$F^E \approx \frac{1.45}{(2z)^2}\ \text{kcal./mol.}$$

$$\text{at } T = 300^\circ\text{K and } x = 0.5$$

If we assume that $Z=4$, F^E becomes $F^E \approx 22$ cal./mol. Although the value 22 cal./mol. obtained above is quite approximate because of the neglect of higher orders than the second, the order of magnitude of the value may not differ from that obtained by rigorous calculation.

Summary

A statistical mechanical theory of solutions consisting of *d*- and *l*-optical isomers is developed based on a new model of optically active molecules, and the excess free energy of the system is also derived and the order of magnitude of this quantity is examined.

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