Thermodynamical Studies on Binary Systems Consisting of Polar and Non-polar Liquids. VI. Refined Calculation of the Electrostatic Part of van Laar Coefficients and Comparison with the Experimental Results

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In a previous paper, the electrostatic parts of the heat mixing polar and non-polar liquids were calculated on the assumptions that the polar molecule was a sphere with isotropic polarizability and that the dipole was located at the center of the sphere. The comparison of these results with those of the experiment for the group of systems containing non-aromatic non-polar liquid showed qualitative agreements. However quantitative agreements were poor, especially for systems containing polar liquid with a large dipole moment.

To ascertain the reason for these poor quantitative agreements, the electrostatic parts of the van Laar coefficients were calculated for two cases, one where the polar molecule was spherical with anisotropic polarizability and the other where it was an ellipsoid with anisotropic polarizability. The dipole was not located at the center of the ellipsoid. These results were compared with the experimental results.

The Effect of the Anisotropy of the Polar Molecule

First, the effect due only to the anisotropy of the polar molecule will be examined by assuming a spherical molecule. In the previous paper[1], the polarizability of the molecule was assumed to be isotropic, and in the subsequent calculations approximate values of the mean polarizability derived from the refractive index of liquids for the sodium D line were used. However, the reaction field of the surrounding medium is always in a direction parallel to the axis of the dipole; therefore, strictly speaking, the polarizability α in the previous paper[1] should be replaced by α_1 polarizability, parallel to the axis of the dipole, if the anisotropy of the polar molecule is to be taken into consideration.

Actual polar molecules are more or less anisotropic; this effect may be significant for the derivatives of benzene or for those molecules having many anisotropic polar groups, such as C≡N. Mean polarizability $\bar{\alpha}$ is defined as

$$\bar{\alpha}=\frac{1}{3}(\alpha_1+\alpha_2+\alpha_3) \tag{1}$$

where α_1, α_2 and α_3 are the polarizabilities along each of three principal axes.

TABLE I. POLARIZABILITY OF POLAR MOLECULES IN UNIT OF 10^{-25} cc./mol.

Substance	α_1	α_2	α_3
Chlorobenzene	155.1	138.2	74.2
Bromobenzene	168.4	121.3	95.6
Benzonitrile	163.8	121.1	84.9
Nitrobenzene	171.6	141.9	74.1
Diethylketone	100.1	126.4	71.5

The values of α_1, α_2 and α_3 for some of the above polar molecules are taken from the literature and are reproduced in Table I, where α_1 is the polarizability along the direction of the dipole and α_2 and α_3 are those perpendicular to the direction of the dipole.

In the same table, the $n_{21}^2/\bar{n}_2^2$ ratio is shown where n_{21} is the refractive index of the polar molecule along the direction of the dipole and $\bar{n}_2$ is the mean value for three axes, expressed as:

$$\frac{n_{21}^2-1}{n_{21}^2+2}=\frac{4}{3}\pi N\alpha_1,\quad \frac{\bar{n}_2^2-1}{\bar{n}_2^2+2}=\frac{4}{3}\pi N\bar{\alpha} \tag{2}$$

It can be seen from Table I that the polarizability parallel to the dipole for benzene derivatives is about 30% larger than the mean polarizability.

It is likely that other molecules, not shown in Table I, have a similar tendency. This suggests that the values of n_2^2 in expression (11) of the previous paper[1] must be replaced with values about 30% larger. This would change the values of integrands g and h the expressions (5) and (6) of the previous paper[1] and, accordingly, that of $\alpha^{\mathrm{el}}_{\mathrm{calcd}}$.

Wilson[2] derived the following expression for the dielectric constant of pure polar liquid and of a solution based on Onsager's model, taking the anisotropy of the polar molecule

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[1] K. Amaya, This Bulletin, 34, 1584 (1961).

[2] J. N. Wilson, *Chem. Revs.*, 25, 377 (1939).

into consideration. For a pure liquid he obtained:

$$\frac{\varepsilon_2-1}{\varepsilon_2}-\frac{3(n_2^2-1)}{2\varepsilon_2+n_2^2}=\frac{4\pi \boldsymbol{N}}{9\boldsymbol{kT}}\mu^2\frac{(2\varepsilon_2+1)(n_{21}^2+2)^2}{2\varepsilon_2+n_{21}^2} \tag{3}$$

where n_{21} is the refractive index of the polar molecule along the dipole axis and n_2 is the mean refractive index.

For a binary solution consisting of polar and non-polar molecules,

$$\frac{\varepsilon_{12}-1}{\varepsilon_{12}}=\frac{4\pi \boldsymbol{N}_2}{9\boldsymbol{kT}}\mu^2\frac{(n_{21}^2+2)^2(2\varepsilon_{12}+1)}{(2\varepsilon_{12}+n_{21})^2}+\frac{3v_2(n_2^2-1)}{2\varepsilon_{12}+n_2^2}+\frac{3v_2(n_1^2-1)}{2\varepsilon_{12}+n_1^2} \tag{4}$$

in which the following notations were used;

$\boldsymbol{N}_2$: the number of the polar molecule in unit volume,
v_2: volume fraction of the polar component,
v_1: volume fraction of the non-polar component,
n_2: mean refractive index of the polar molecule,
n_1: mean refractive index of the non-polar molecule,
n_{21}: refractive index along the dipole axis of the polar molecule,
ε_{12}: dielectric constant of the solution.

Following a procedure similar to that used before, we can express ε_{12} by using values for pure components; the following expression is obtained:

$$\frac{\varepsilon_{12}-1}{\varepsilon_{12}}=v_2\cdot\frac{(2\varepsilon_2+n_{21}^2)^2}{2\varepsilon_2+1}\times\left(\frac{\varepsilon_2-1}{\varepsilon_2}-\frac{3n_2^2-1}{2\varepsilon_2+n_2^2}\right)\cdot\frac{2\varepsilon_{12}+1}{(2\varepsilon_{12}+n_{21}^2)^2}+\frac{3v_2(n_2^2-1)}{2\varepsilon_{12}+n_2^2}+\frac{3(1-v_2)(n_1^2-1)}{2\varepsilon_{12}+n_1^2} \tag{5}$$

where ε_1 and ε_2 are the dielectric constants of non-polar and polar liquids respectively.

By the use of the above expression, the volume fraction of the polar component v_2' for any value of ε_{12} can be determined from the data of the pure liquids. To see how the anisotropy of the polar molecule affects the calculated values of the volume fraction, the values of v_2' * for chlorobenzene-cyclohexane and nitrobenzene-cyclohexane systems were compared with v_2, for which the anisotropy of the polar molecule is not taken into consideration. It was found that the differences were of the order of 0.01.

By using these values of the volume fraction v_2' and by replacing the values of n_2 with those along the dipole axis, n_{21}, van Laar coefficients $\alpha_{\text{calcd}}^{\text{el}'}$ were calculated for the above two systems and are shown in Table II. The $\alpha_{\text{calcd}}^{\text{el}'}/\alpha_{\text{calcd}}^{\text{el}}$ and $\alpha_{\text{calcd}}^{\text{el}'}/\alpha_{\text{obs}}^{\text{el}}$ ratios for $v_2=1$, 0.75, 0.5, 0.25 and 0 are also shown in Table III.

TABLE II. THE CALCULATED VALUES OF THE ELECTROSTATIC PART OF VAN LAAR COEFFICIENT, $\alpha^{\text{el}'}$, TAKING THE ANISOTROPY OF POLAR MOLECULES INTO ACCOUNT

System	v_2'	$\alpha^{\text{el}'}$ (joul./cc.)
Chlorobenzene + Cyclohexane	1.00	8.50
	0.829	8.86
	0.651	9.68
	0.461	10.68
	0.251	12.22
	0	13.76
Nitrobenzene + Cyclohexane	1.00	20.91
	0.811	24.50
	0.622	31.51
	0.431	43.97
	0.236	71.10
	0.076	131.84
	0	175.31

TABLE III. RATIO OF THE VALUES OF ELECTROSTATIC PART OF VAN LAAR COEFFICIENTS CALCULATED ACCORDING TO WILSON'S FORMULA TO THAT CALCULATED ACCORDING TO ONSAGER'S FORMULA $\alpha^{\text{el}'}/\alpha^{\text{el}}$

System	Volume fraction of polar component	$\alpha^{\text{el}'}/\alpha^{\text{el}}$
Chlorobenzene + Cyclohexane	1.00	1.183
	0.75	1.195
	0.50	1.170
	0.25	1.175
	0	1.143
Nitrobenzene + Cyclohexane	1.00	1.530
	0.75	1.511
	0.50	1.477
	0.25	1.404
	0	1.242

It can be seen from the above results that the introduction of the anisotropy of polarizability makes the calculated values of α^{el} in these two systems larger by 10 to 50%. For other systems, similar changes may be expected. The agreement between the calculated and observed values is not very much improved by consideration of the anisotropy.

The Effect of the Position of the Dipole on the Molecule and on Molecular Shape

The calculations were based on the assumptions that the molecule was spherical and that the dipole was located at the center of the

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* v_2' designates the value of v_2 obtained by taking into consideration the anisotropy of the polar molecules.

molecule. The deviations in the position of the dipole from the center of the molecule and the deviation in molecular shape from a sphere will be discussed here to see how they affect the results.

First, the deviation in the position of the dipole from the center of the molecule will be considered. Assuming that the radius of the sphere is a, and that the dipole point is located at a distance s from the center of the sphere, Böttcher[3] derived the following expression for the electrostatic free energy, W, of a non-polarizable dipole whose dipole moment is μ, in the dielectric medium as a function of ε, the dielectric constant of the medium, and the ratio s/a:

$$W=-\frac{\varepsilon-1}{2\varepsilon}\frac{\mu^2}{a^3}\times\left[\sum_{l=0}^{\infty}\frac{l^2(l+1)(2\varepsilon+1)}{2(\varepsilon l+\varepsilon+l)}\left(\frac{s}{a}\right)^{2l-2}\right] \tag{6}$$

When the dipole is at the center of the sphere, the value in the bracket become unity; hence, the correction factor for the deviation in the position of the dipole is obtained by evaluating the value in the bracket.

For actual molecules, however, their dipoles are polarizable and their molecular shapes are not spherical. It may be assumed that for the polarizable dipole the correction factor for the deviation in the position of the dipole from the center of the sphere does not differ from that for the non-polarizable dipole; it may also be assumed that for an ellipsoidal molecule the correction factor for the ellipsoid does not differ from that for the sphere. Instead of s/a in the above formula, we may take the ratio s_i/l_i, where s_i is the distance between the center of the ellipsoid and the projection of the center of the dipole on each principal axis i, and l_i is half the length, along the corresponding principal axis i. By using the values for van der Waals' radii and the bonding radii of atoms found in the literature, the length along each principal axes, $2a$, $2b$ and $2c$, of the molecule can be obtained. By assuming that the molecule is an ellipsoid with principal axes $2a$, $2b$ and $2c$ and that the dipole is located at the center of that bond, the results shown in Table IV are obtained.

In some molecules the centers of the dipoles are not on one of their three principal axes and the direction of the dipole does not coincide with that of one of three principal axes. In these cases, the circumstances may be changed, but this problem will not be considered here in detail.

By using the values in Table IV, the correction factors r_p were calculated at eleven or twelve points of the dielectric constants for each system. Only the extreme values ($v_2=1$ and 0) are shown in Table V.

TABLE IV. VALUES OF a, b, c, s_a/a, s_b/b and s_c/c FOR THE POLAR MOLECULES ($a>b>c$)

Kind of polar molecule	$2a$ Å	$2b$ Å	$2c$ Å	s_a/a	s_b/b	s_c/c
Chlorobenzene	8.6	6.7	3.7	0.37	0	0
Bromobenzene	8.9	6.7	3.9	0.35	0	0
Benzonitrile	9.3	6.7	3.7	0.54	0	0
Nitrobenzene	8.6	6.7	3.1	0.51	0	0
n-Butyl chloride	9.0	4.5	4.1	0.44	0.02	0
n-Butyl cyanide	9.2	4.8	4.1	0.57	0.25	0
Diethyl ketone	9.1	5.4	4.1	0	0.26	0
Cyclohexanone	7.5	7.1	5.1	0.50	0.24	0
Chlorocyclohexane	8.6	7.1	5.1	0.39	0.03	0
Bromocyclohexane	8.8	7.1	5.1	0.36	0.02	0

It can be seen from these results that the effect of the deviation in the position of the dipole from the center of the molecule is considerable and that the correction factors are always greater than unity and amount to as much as about 4 for *n*-butyl cyanide.

Next, the effect of the deviation in the molecular shape from a sphere will be considered. For an ellipsoid with principal axes $2a$, $2b$ and $2c$, the reaction field factor along the direction of the principal axis a, f_a, in a medium with a dielectric constant ε is expressed as:

$$f_a=\frac{3}{abc}A_a(1-A_a)(\varepsilon-1)/\{\varepsilon+(1-\varepsilon)A_a\}$$

$$A_a=\frac{abc}{2}\int_0^{\infty}\frac{\mathrm{d}x}{(x+a^2)\sqrt{(x+a^2)(x+b^2)(x+c^2)}} \tag{7}$$

For other axes similar expressions were obtained.

For an ellipsoid $a\geqq b\geqq c$, A_a A_b and A_c are expressed as:

$$A_a=\frac{(b/a)\cdot(c/a)}{\{1-(c/a)^2\}^{3/2}}\cdot\frac{1}{k^2}\{F(k,\rho)-E\ (k,\rho)\} \tag{8}$$

$$A_b=\frac{(b/a)\cdot(c/a)}{\{1-(c/a)^2\}^{3/2}}\cdot\frac{1}{k'^2}\left\{\frac{E(k,\rho)-k'^2F(k,\rho)}{k^2}-\frac{(c/a)\cdot\sqrt{1-(c/a)^2}}{b/a}\right\} \tag{9}$$

$$A_c=\frac{(b/a)\cdot(c/a)}{\{1-(c/a)^2\}^{3/2}}\cdot\frac{1}{k'^2}\left\{\frac{b}{a}\cdot\tan\rho-E(k,\rho)\right\} \tag{10}$$

where

$$k_2=\{1-(b/a)^2\}/\{1-(c/a)^2\}$$

$$k'^2=1-k^2$$

$$\sin^2\rho=1-(c/a)^2$$

$$F(k,\rho)=\int_0^{\rho}\frac{\mathrm{d}\theta}{\sqrt{1-k^2\sin^2\theta}}$$

$$E(k,\rho)=\int_0^{\rho}\sqrt{1-k^2\sin^2\theta}\;\mathrm{d}\theta$$

For a spherical molecule A becomes 1/3, for elongated molecules, the values of A are smaller than 1/3, and for oblate molecules, they are greater than 1/3. Therefore, the reaction field factor is smaller than that for a shpere when A is smaller than 1/3, and is larger than that of a sphere when A is larger than 1/3.

When the direction of the dipole does not coincide with one of the principal axes, the values of A for the direction of the dipole moment, A_μ, may be approximated as

$$A_\mu=\sum A_i\cos^2\theta_{\mu i} \qquad (11)$$

where $\theta_{\mu i}$ is the angle between the direction of the dipole moment μ and that of the principal axis i. Using the molecular dimensions shown in Table IV, the values of A for each polar molecule have been calculated and are shown in Table VI. If an ellipsoidal model is assumed and if also an anisotropy of the polarizability of the polar molecule is taken into consideration, integrand g in expression (2) in the previous paper[1] must be replaced by g'

$$g'=f_{\mu e}/(1-f_{\mu e}\alpha_\mu) \qquad (12)$$

where $f_{\mu e}$ is the reaction field factor along the direction of the dipole of a non-polarizable ellipsoid and α_μ is the polarizability along the direction of the dipole. α_μ is expressed as

$$\alpha_\mu=\sum_i\alpha_i\cos^2\theta_{\mu i} \qquad (13)$$

where α_i is the polalizability along the principal axis i and $\theta_{\mu i}$ is the same as has been mentioned above.

α_i's are calculated from the bond polarizability and molecular structure when the experimental values are not available; thus the ratio $\alpha_\mu/\overline{\alpha}$ was obtained, where $\overline{\alpha}$ is the mean polarizability, $\overline{\alpha}=(1/3)\cdot\sum_i\alpha_i$.

The ratios of $\alpha_\mu/\bar{\alpha}$ are shown in Table VI.

The correction factor r_s due to the deviation of the shape of the molecule from sphere r_s for integrand g of the expression (2) in the previous paper[1] may be expressed as

$$r=\frac{g'}{g}=\frac{f_\mu/(1-f_{\mu e}\alpha_\mu)}{f_s/(1-f_s\cdot\overline{\alpha})} \qquad (14)$$

where $f_s=\{(2\varepsilon-2)/(2\varepsilon+1)\}\cdot 1/a^2$, and f_s relates to g as $g=f_s/(1-f_s\alpha)$.

By using the above values of $\alpha_\mu/\overline{\alpha}$ and $\overline{\alpha}=(n_D^2-1)/(n_D^2+2)$, and assuming that a^3 in f_s, the reaction field factor for a sphere, is equal to *abc* in f_e, the values of r_s were calculated at eleven or twelve points of dielectric constant for each system, only extreme values are shown in Table V.

The effect of deviation in molecular shape from a sphere and that of the deviation in the position of the dipole from the center of the molecule is simultaneously represented as a product of both. The products of both correction factor are also represented in Table V.

It may be assumed that the resultant correction factors for h are the same as that for g. In calculating the van Laar coefficient the integrand h for a definite value of ε is multiplied by the resultant correction factor for the corresponding values of ε, and the corrected h is integrated with the volume fraction which is obtained by solving the equation relating volume fraction and ε derived according to the ellipsoidal model. However, as the resultant correction factor obtained above for g varies very little with the concentration, the approximate values of the refined van Laar coefficient

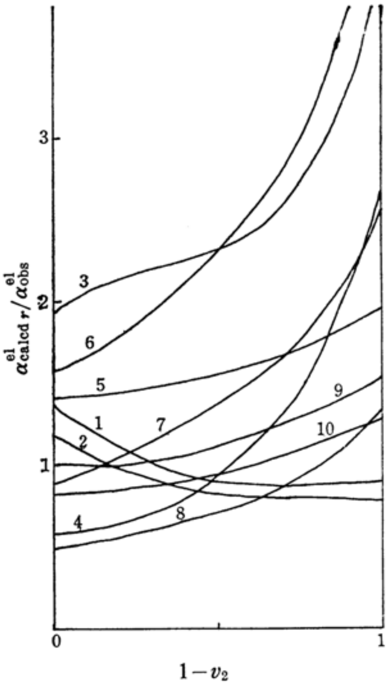

Fig. 1. Ratio of $\alpha^{el}_{calcd\,r}/\alpha^{el}_{obs}$ plotted against volume fraction.

1. Chlorobenzene-Cyclohexane
2. Bromobenzene-Cyclohexane
3. Benzonitrile-Cyclohexane
4. Nitrobenzene-Cyclohexane
5. *n*-Butyl chloride-Cyclohexane
6. *n*-Butyl cyanide-Cyclohexane
7. Cyclohexanone-Cyclohexane
8. Diethyl ketone-Cyclohexane
9. Chlorocyclohexane-Methylcyclohexane
10. Bromocyclohexane-Methylcyclohexane

TABLE V. THE CORRECTION FACTOR DUE TO MOLECULAR SHAPE AND POSITION OF THE DIPOLE OF POLAR MOLECULES FOR THE ELECTROSTATIC ENERGY OF THEIR SOLUTIONS

System	v_2	Correction factor		
		Due to molecular shape, r_s	Due to position of the dipole, r_p	Resultant r_r
Chlorobenzene	1	0.5075	1.7444	0.8852
+				
Cyclohexane	0	0.5748	1.7134	0.9848
				mean 0.9231
Bromobenzene	1	0.5769	1.6405	0.9463
+				
Cyclohexane	0	0.6388	1.6149	1.0316
				mean 0.9797
Benzonitrile	1	0.5586	3.6096	2.0164
+				
Cyclohexane	0	0.6535	3.4128	2.2304
				mean 2.0716
Nitrobenzene	1	0.4705	3.0977	1.4574
+				
Cyclohexane	0	0.5768	2.9399	1.6959
				mean 1.5100
n-Butyl chloride	1	0.7327	2.2435	1.6439
+				
Cyclohexane	0	0.7916	2.1796	1.7254
				mean 1.6712
n-Butyl cyanide	1	0.7025	4.2669	2.9975
+				
Cyclohexane	0	0.7759	4.0187	3.1182
				mean 8.0309
Cyclohexanone	1	0.9789	2.9404	2.8783
+				
Cyclohexane	0	0.9826	2.8046	2.7557
				mean 2.8446
Diethyl ketone	1	1.2048	1.3137	1.5827
+				
Cyclohexane	0	1.1168	1.2959	1.4474
				mean 1.5408
Chlorocyclohexane	1	0.7722	1.8695	1.4437
+				
Methylcyclohexane	0	0.8257	1.8254	1.5071
				mean 1.4653
Bromocyclohexane	1	0.7500	1.6971	1.2728
+				
Methylcyclohexane	0	0.8072	1.6625	1.3420
				mean 1.2967

TABLE VI. VALUES OF A_a, A_b, A_c, A_μ AND $\alpha_\mu/\overline{\alpha}$ FOR THE POLAR MOLECULES

Kind of polar molecule	A_a	A_b	A_c	A_μ	$\alpha_\mu/\overline{\alpha}$
Chlorobenzene	0.1756			0.1756	1.266
Bromobenzene	0.1953			0.1953	1.312
Benzonitrile	0.1993			0.1993	1.328
Nitrobenzene	0.1756			0.1756	1.328
n-Butyl chloride	0.1646	0.4080		0.2486	1.095
n-Butyl cyanide	0.1679	0.3852		0.2430	1.127
Diethyl ketone	0.3875			0.3875	1.007
Cyclohexane	0.2660		0.4315	0.3232	1.057
Chlorocyclohexane	0.2420		0.4506	0.2621	1.095
Bromocyclohxane	0.2343		0.4549	0.2556	1.110

TABLE VII. THE CALCULATED AND THE OBSERVED VALUES OF $d\alpha/dv_2$ AT $v_2=0$

System	$(d\alpha/dv_2)_{v_2=0}$ calcd.	Refined calcd.	Obs.
Chlorobenzene-Cyclohexane	6.688	6.174	7.53
Bromobenzene-Cyclohexane	6.505	6.373	10.02
Benzonitrile-Cyclohexane	392.5	813.1	87.44
Nitrobenzene-Cyclohexane	601.0	907.5	~90
n-Butyl chloride-Cyclohexane	25.58	42.75	13.50
n-Butyl cyanide-Cyclohexane	349.5	1059.3	54.01
Cyclohexanone-Cyclohexane	143.9	409.3	57.44
Diethyl ketone-Cyclohexane	127.2	196.0	60.62
Chlorocyclohexane-Methylcyclohexane	17.95	26.30	17.95
Bromocyclohexane-Methylcyclohexane	16.83	21.82	6.61

may be obtained by multiplying the values formerly calcurated for the spherical model by a constant, that is, the mean values of the resultant correction factors in Table V averaged over the whole concentration, if the difference between v_2 calculated by a spherical model and that calculated by an ellipsoidal model is disregarded as small. By assuming that these approximations are permissible, the refined van Laar coefficients $\alpha^{el}_{calcd\,r}$ are obtained. The ratio $\alpha^{el}_{calcd\,r}/\alpha^{el}_{obs}$ is plotted in Fig. 1.

It will be seen from the results that in general, the agreement between the refined calculation and the experimental results is similar to those of the former calculation for systems of polar liquids of a small dielectric constant, but for systems of polar liquids of a large dielectric constant the agreement is even poorer than before. Since the values of α^{el}_{obs} are correlated to the assumed values of α^{n-el} by the relation $\alpha_{obs}=\alpha^{n-el}+\alpha^{el}_{obs}$, the impropriety of the assumed values of α^{n-el} affect α^{el}_{obs}, and hence $\alpha^{el}_{calcd}/\alpha^{el}_{obs}$. However, the values of $d\alpha^{el}/dv$ are not affected by the assumed values of α^{n-el} whatever they may be, provided that α^{n-el} is independent of the concentration. The calculated values of $d\alpha^{el}/dv_2$ at $v_2=0$ obtained by the former calculation and by the refined calculation are shown in Table VII, together with the experimental values. It can be seen from the table that the agreement is not improved.

It may be concluded that the main sources of the poor agreement of the former theory with the experimental results, especially for solutions of polar liquids with a large dielectric constant, is not the assumption of a spherical molecule with its dipole at the center.

To make clear what is responsible for the poor quantitative agreement between theory and experiment in the heats of mixing a polar liquid (especially one with a large dielectric constant) and a non-polar liquid, the following points have to be considered from a theoretical as well as from an experimental point of view:

(1) To consider the orientational effect of polar molecules in pure liquids and in their concentrated solutions, due to dipole and anisotropy similar to that which is observed for toluene molecules in its solutions with polar molecules and to examine the assumption that the van Laar coefficient due to the non-electrostatic part of the energy is constant over the whole concentration.

(2) To examine the assumption that the microscopic dielectric constant near the polar molecule is the same as the microscopic one.

(3) To employ an extended dipole instead of a point dipole one in deriving the theory.

(4) To eliminate the error caused by using calculated values of the dielectric constant of solutions, by making use of the observed values of dielectric constants and of the temperature dependence of solutions

Summary

The electrostatic parts of van Laar coefficients for binary systems of polar and non-polar liquids were calculated, assuming that (1) the polar molecule is anisotropic in polarizability, (2) that the polar molecule is an ellipsoid, and (3) that the dipole is a point dipole and its position is not at the center of the molecule.

The results were compared with the experimental results.

The agreement between the experimental values and the calculated values based on the refined model cannot be said to have been improved compared with the previous results, in which the calculations were made based on the much simpler model in which the polar molecule was spherical and isotropic, and the dipole was at the center of the sphere.

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