Thermodynamical Studies on Binary Systems Consisting of Polar and Non-polar Liquids. IV. Estimation of the Electrostatic Part of the Excess Enthalpy from the Observed Values aud Comparison with the Calculated Values

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In a previous paper[1], the author calculated the electrostatic part of the excess enthalpy of binary systems composed of polar and non-polar liquids according to Onsager's model. In this paper the observed values of these quantities have been derived under reasonable assumptions and are compared with the calculated values.

The Principle of the Estimation of the Electrostatic Part of the Excess Enthalpy from the Experimental Results

In order to derive the electrostatic part of the excess enthalpy due only to the permanent dipole of the polar molecule from the experimental result of the heat of mixing, the non-electrostatic part of the excess enthalpy must be estimated under reasonable assumptions and subtracted from the experimental value, since the observed excess enthalpy contains not only the electrostatic but also the non-electrostatic part.

As a first approximation, it may be assumed that the intermolecular interaction enery of polar molecules is the sum of the non-electrostatic part of the energy due to dispersion forces and the electrostatic one due to dipoles if higher multipoles are neglected.

From this assumption the cohesive energy for 1 mol. of pure polar liquid, $\varDelta U_2$, may be given by

$$\varDelta U_2=\varDelta U_2^{\mathrm{el}}+\varDelta U_2^{\mathrm{n-el}} \tag{1}$$

where $\varDelta U_2^{\mathrm{el}}$ and $\varDelta U_2^{\mathrm{n-el}}$ are the electrostatic and the non-electrostatic part of cohesive energy respectively.

Since the electrostatic intermolecular energy is absent in non-polar liquids, the cohesive energy for non-polar liquid $\varDelta U_1$ is given by the non-electrostatic intermolecular energy due to dispersion forces of non-polar molecules:

$$\varDelta U_1=\varDelta U_1^{\mathrm{n-el}} \tag{2}$$

Further, if the non-electrostatic part of the energy due to dispersion forces is assumed to be the sum of the energy due to dispersion forces of the nearest neighbor pairs, then for 1 mol. of polar liquid $\varDelta U_2^{\mathrm{n-el}}$ is given by

$$\varDelta U_2^{\mathrm{n-el}}=1/2\cdot N_A z\omega_{22} \tag{3}$$

and similarly for 1 mol. of non-polar liquid,

$$\varDelta U_1^{\mathrm{n-el}}=1/2\cdot N_A z\omega_{11} \tag{4}$$

where N_A is Avogadro's number, z is the number of the nearest neighbors and ω_{22} and ω_{11} are the non-electrostatic part of interaction energy due to dispersion forces of the nearest neighbor pairs of polar and non-polar molecules respectively.

When 1 mol. of the solution is formed from x_2 mole of polar liquid and $(1-x_2)$ mol. of non-polar liquid, both liquids being composed of molecules of similar size, the total energy of the system $\varDelta U_{12}$ is given by

$$\varDelta U_{12}=\frac{1}{2}x_2^2 N_A z\omega_{22}+x_2(1-x_2)N_A z\omega_{12}+\frac{1}{2}(1-x_2)^2 N_A z\omega_{11}+\varDelta U_{12}^{\mathrm{el}} \tag{5}$$

where ω_{12} is the non-electrostatic part of the nearest neighbor pair interaction energy of the pair consisting of polar and non-polar molecules and $\varDelta U_{12}^{\mathrm{el}}$ is the electrostatic part of the energy due to dipoles for 1 mol. of the solution. Thus the excess energy U^{E} is given by

$$U^{\mathrm{E}}=x_2(1-x_2)N_A z\omega+\varDelta U_{12}^{\mathrm{el}}-x_2\varDelta U_2^{\mathrm{el}} \tag{6}$$

where ω is the part of interchange energy due to dispersion forces given by

$$2\omega=2\omega_{12}-\omega_{22}-\omega_{11} \tag{7}$$

In a similar way the electrostatic part of the excess energy due to dipole-dipole interaction as well as the non-electrostatic contribution due to dispersion forces may be expressed as a function of volume fraction v_2 of the polar liquid:

$$U^{\mathrm{E}}=V\alpha^{\mathrm{n-el}}v_2(1-v_2)+\varDelta U_{12}^{\mathrm{el}}(v_2)-v_2\cdot\varDelta U_2^{\mathrm{el}} \tag{8}$$

where V is the volume of 1 mol. of the solution.

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[1] K. Amaya, This Bulletin, 34, 1349 (1961).

TABLE I. VALUES OF $\alpha^{\mathrm{el}}_{\mathrm{obs}}(0)$, $\alpha^{\mathrm{el}}_{\mathrm{obs}}(1)$, $\Delta\alpha^{\mathrm{el}}_{\mathrm{obs}}$ and $\alpha^{\mathrm{el}}_{\mathrm{obs}}(0)/\alpha^{\mathrm{el}}_{\mathrm{obs}}(1)$ FOR THE SYSTEMS IN WHICH NON-POLAR COMPONENTS ARE NON-AROMATIC

System	$\alpha^{\mathrm{el}}_{\mathrm{obs}}(0)$ joul./cc.	$\alpha^{\mathrm{el}}_{\mathrm{obs}}(1)$ joul./cc.	$\Delta\alpha^{\mathrm{el}}_{\mathrm{obs}}$ joul./cc.	$\alpha^{\mathrm{el}}_{\mathrm{obs}}(0)/\alpha^{\mathrm{el}}_{\mathrm{obs}}(1)$
Chlorobenzene—Cyclohexane	12.5	4.9	7.6	2.54
Bromobenzene—Cyclohexane	15.7	6.1	9.6	2.58
Benzonitrile—Cyclohexane	65.6	25.0	40.6	2.62
Nitrobenzene—Cyclohexane	75	37	38	2.03
Cyclohexanone—Cyclohexane	54.9	31.8	23.1	1.73
Diethylketone—Cyclohexane	54.4	28.9	25.5	1.89
Methylpropylketone—Cyclohexane	56.9	32.5	24.4	1.75
n-Butylchloride—Cyclohexane	21.8	11.2	10.6	1.95
n-Butylcyanide—Cyclohexane	59.2	33.9	25.3	1.75
Chlorocyclohexane—Methylcyclohexane	16.0	9.95	6.0_5	1.61
Bromocyclohexane—Methylcyclohexane	17.5	11.3	6.2	1.55
cis-Dichloroethylene—*trans*-Dichloroethylen	10.4	5.4	5.0	1.95
Pyridine—1,4-Dioxane	4.7	<1.9	>2.8	2.24

It may be assumed that $\alpha^{\mathrm{n-el}}$, the contribution of dispersion forces to the van Laar coefficient is constant over the whole concentration range, because the coefficients α for binary systems of non-polar liquids are nearly constant. In addition it is also assumed that there is no volume change on mixing. Then U^{E} is equal to H^{E}:

$$U^{\mathrm{E}}=H^{\mathrm{E}}=V\alpha^{\mathrm{n-el}}v_2(1-v_2)+H^{\mathrm{E-el}} \tag{9}$$

$$U^{\mathrm{E-el}}=H^{\mathrm{E-el}}=U^{\mathrm{E-el}}-\Delta U_{12}{}^{\mathrm{el}}(v_2)-v_2\cdot\Delta U_2{}^{\mathrm{el}} \tag{10}$$

Further, if the electrostatic part is expressed in the form

$$H^{\mathrm{E-el}}=V\alpha^{\mathrm{el}}v_2(1-v_2) \tag{11}$$

then

$$H^{\mathrm{E}}=V(\alpha^{\mathrm{n-el}}+\alpha^{\mathrm{el}})v_2(1-v_2) \tag{12}$$

where α^{el} is the electrostatic contribution to α.

The Estimation of $\alpha^{\mathrm{n-el}}$, Non-electrostatic Part of α

The values of α^{el} can be obtained if the values of $\alpha^{\mathrm{n-el}}$ are estimated under reasonable assumptions. And for estimating the non-electrostatic part of the heat of mixing, the following procedures are employed:

(1) The Systems of Cyclohexane—Aliphatic Polar Molecule. — For cyclohexane—*n*-hexane system the heat of mixing per mole of cyclohexane at the extreme dilution is about 573 joul./mol.[2] corresponding to the value of 5.3 joul./cc. for α. Since for non-polar liquid systems the values of α do not vary with concentration, it may be reasonable to use the above value over all the concentration range. Even for the binary systems of cyclohexane and polar aliphatic hydrocarbon derivatives, it may be permissible, as an approximation, to take the value of 5.3 joul./cc. non-electrostatic part of α, neglecting the difference for between CH_3, CH_2 and the polar groups.

(2) The Systems of Cyclohexane—Benzene Derivative.—In (1) the observed values of the electrostatic part of α at the two extreme concentrations of $v_2=1$ and 0, $\alpha^{\mathrm{el}}_{\mathrm{obs}}(1)$ and $\alpha^{\mathrm{el}}_{\mathrm{obs}}(0)$, are obtained by subtracting the value of 5.3 joul./cc. from the observed values at the corresponding concentrations. If the ratios, $\alpha^{\mathrm{el}}_{\mathrm{obs}}(0)/\alpha^{\mathrm{el}}_{\mathrm{obs}}(1)$, are calculated, they are found to lie between 2.0 and 1.5 as shown in Table I. Accordingly, if may be permissible to approximate the corresponding ratio in the cyclohexane—toluene system to be 2. Then, by empolying the observed value of $\alpha_{\mathrm{obs}}(0)=24.78$ joul./cc., $\alpha_{\mathrm{obs}}(1)=20.81$ joul./cc. for this system, the non-electrostatic part of α of 17.0 joul./cc. is obtained. As an approximation, neglecting the difference between CH_3 group of toluene and polar groups in other benzene derivatives, it may be plausible to assume the value of 17.0 joul./cc. as the non-electrostatic part of α for cyclohexane—benzene derivative systems.

The ratios of $\alpha^{\mathrm{el}}_{\mathrm{obs}}(0)/\alpha^{\mathrm{el}}_{\mathrm{obs}}(1)$ for the systems in which the non-polar components are non aromatic are shown in Table I.

It is seen from the table that the values of the ratio $\alpha^{\mathrm{el}}_{\mathrm{obs}}(0)/\alpha^{\mathrm{el}}_{\mathrm{obs}}(1)$ for the aromatic polar molecules are nearly equal to about 2, but slightly larger than those for non-aromatic molecules.

(3) The Systems of Cyclohexane—Cyclohexanone, Methylcyclohexane — Harocyclohexane and *cis*- and *trans*-Dichloroethylene Systems.—It is assumed that the non-electrostatic part of α is equal to zero because of the similarity of the two components.

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[2] Landolt-Bernstein, Physikalische-Chemiche Tabellen, III. Erg., p. 2826.

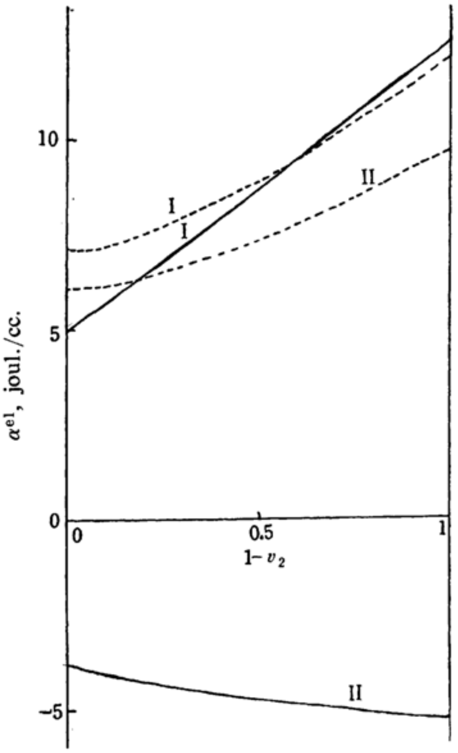

Fig. 1.1. Chlorobenzene—cyclohexane (I) and chlorobenzene—toluene (II) systems.

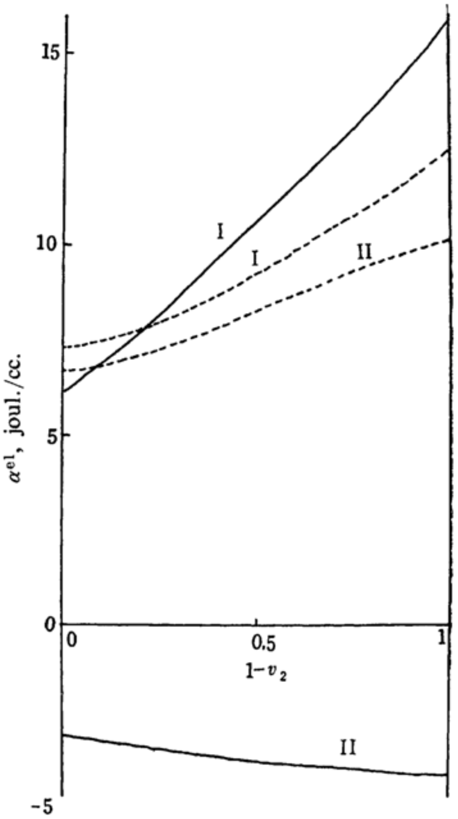

Fig. 1.2. Bromobenzene—cyclohexane (I) and bromobenzene—toluene (II) systems.

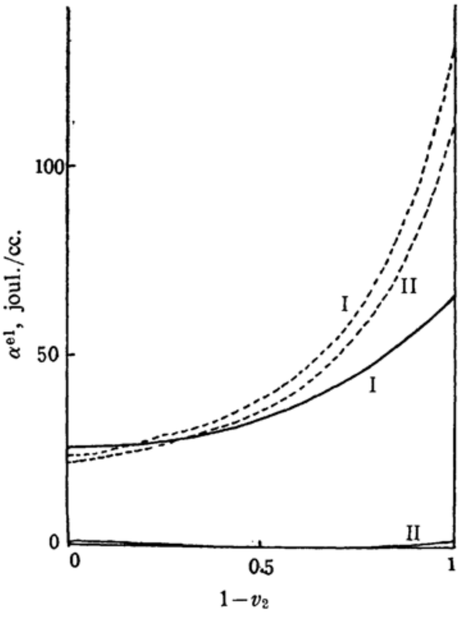

Fig. 1.3. Benzonitrile — cyclohexane (I) and benzonitrile—toluene (II) systems.

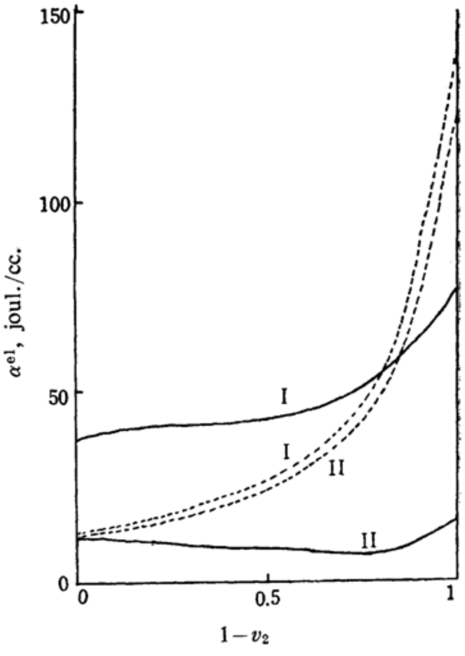

Fig. 1.4. Nitrobenzene — cyclohexane (I) and nitrobenzene—toluene (II) systems.

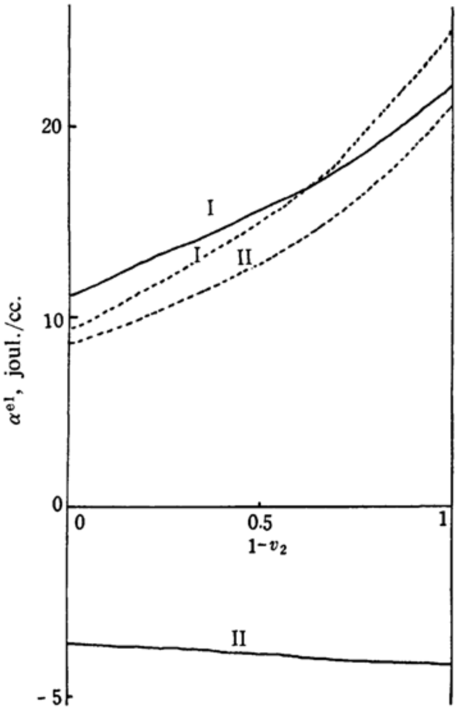

Fig. 1.5. Butylchloride — cyclohexane (I) and butylchloride—toluene (II) systems.

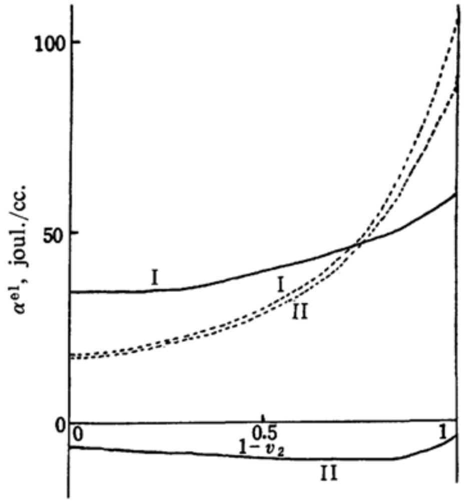

Fig. 1.6. Butylcyanide — cyclohexane (I) and butylcyanide—toluene (II) systems.

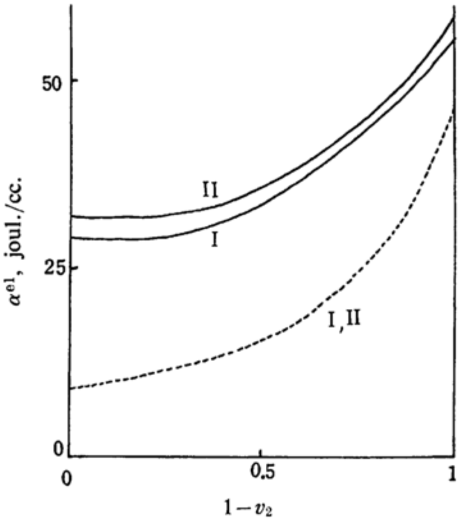

Fig. 1.7. Diethylketone — cyclohexane (I) and methylpropylketone — cyclohexane (II) systems.

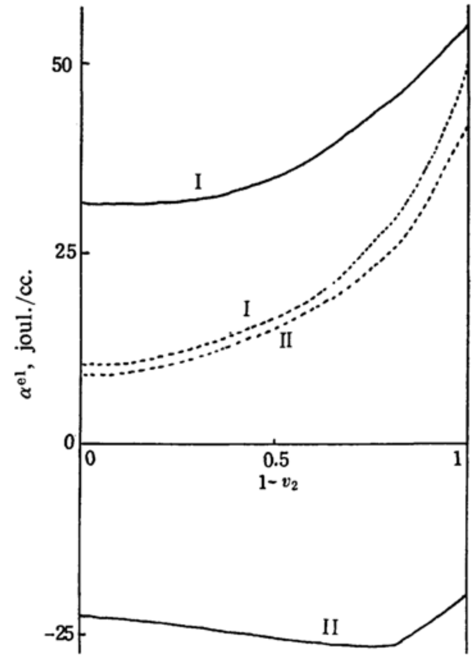

Fig. 1.8. Cyclohexanone—cyclohexane (I) and cyclohexanone—toluene (II) systems.

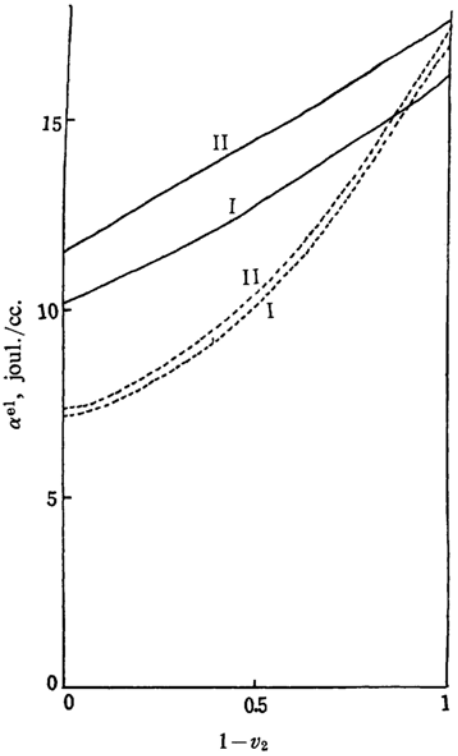

Fig. 1.9. Chlorocyclohexane—methylcyclohexane (I) and bromocyclohexane—methylcyclohexane (II) systems.

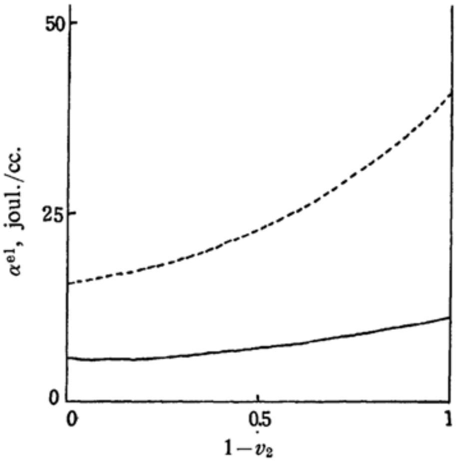

Fig. 1.10. *cis*-Dichloroethylene—*trans*-dichloroethylene system.

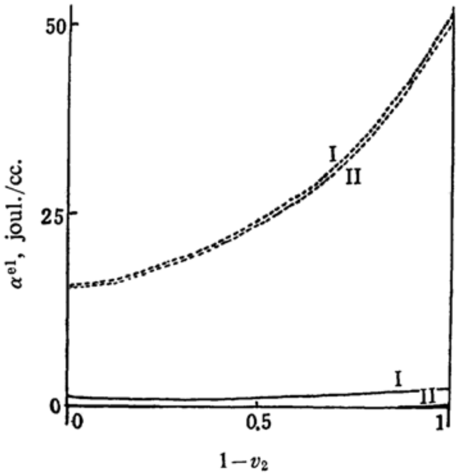

Fig. 1.11. Pyridine—1,4-dioxane (I) and pyridine—benzene (II) systems.

Fig. 1.1—1.11. The observed and the calculated values of electrostatic part of van Laar coefficient α^{el} plotted against volume fraction.
—— Observed ---- Calculated

For the systems in which non-polar components are aromatic such as toluene or benzene, α^{n-el}, the non-electrostatic part of α, is estimated as follows.

(4) The Systems of Toluene—Aromatic Polar Molecule.—For the systems of toluene—benzene derivatives and of benzene—pyridine, the α^{n-el} are assumed to be zero for their structural similarity.

(5) The Systems of Toluene—Aliphatic Polar Molecule. — For butylchloride — toluene, and butylcyanide—toluene systems, the values of α^{n-el} are estimated from the data of heat of mixing for the toluene—*n*-heptane system[3], by neglecting the differences between the polar group and CH_3 or CH_2 groups as before. For the present cases the value of α for *n*-heptane (1.5 joul./cc.) are assumed to be α^{n-el}.

For the cyclohexanone-toluene system α^{n-el} is assumed to be 17.0 joul./cc. as before.

Results and Discussion

The values of the electrostatic part of the van Laar coefficient α^{el}_{obs} were plotted against volume fraction with solid lines in Figs. 1.1—1.11.

Before comparing them with the calculated values, it will be examined whether there exist any regularity between these values and dielectric constants of the polar component or not.

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[3] Landolt-Bernstein, Physikalische-Chemische Tabellen, H. W. II, p. 1567.

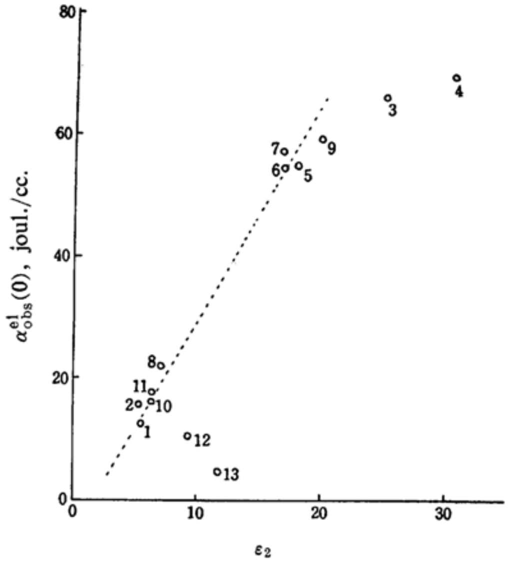

Fig. 2.

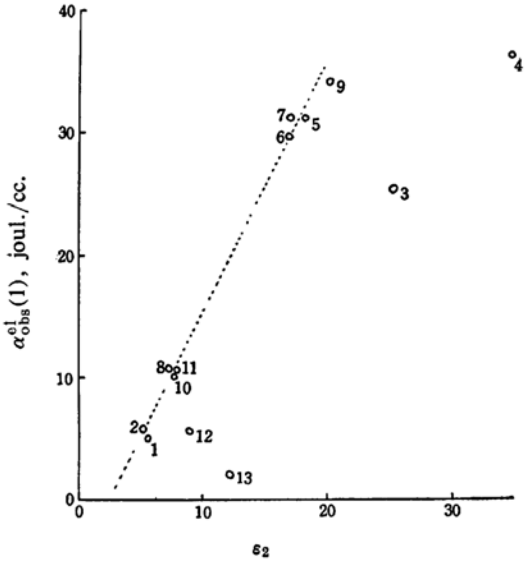

Fig. 3.

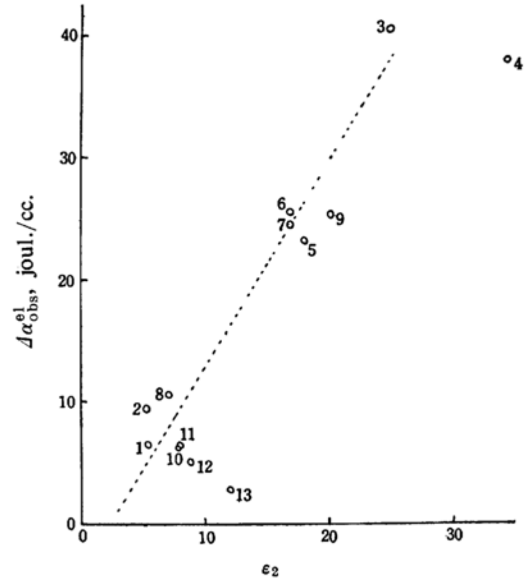

Fig. 4.

Figs. 2, 3 and 4. The plots of observed values of electrostatic part of van Laar coefficients at concentration $v_2=0$ and $v_2=1$ and their difference, $\alpha^{\rm el}_{\rm obs}(0)$, $\alpha^{\rm el}_{\rm obs}(1)$ and $\Delta\alpha^{\rm el}_{\rm obs}$ respectively vs. dielectric constant of polar components ε_2 for systems with non-aromatic non-polar components.

1. Chlorobenzene—Cyclohexane
2. Bromobenzene—Cyclohexane
3. Benzonitrile—Cyclohexane
4. Nitrobenzene—Cyclohexane
5. Cyclohexanone—Cyclohexane
6. Diethylketone—Cyclohexane
7. Methylpropylketone—Cyclohexane
8. *n*-Butylchloride—Cyclohexane
9. *n*-Butylcyanide—Cyclohexane
10. Chlorocyclohexane—Methylcyclohexane
11. Bromocyclohexane—Methylcyclohexane
12. *cis*-Dichloroethylene—*trans*-Dichloroethylene
13. Pyridine—1,4-Dioxane

For systems in which non-polar components are non-aromatic such as cyclohexane and methyl cyclohexane etc.,. the values of $\alpha^{\rm el}_{\rm obs}$ at $v_2=1$ and $v_2=0$, $\alpha^{\rm el}_{\rm obs}(1)$ and $\alpha^{\rm el}_{\rm obe}(0)$ respectively, are shown in Table I.

The difference of $\alpha^{\rm el}_{\rm obs}(0)$ and $\alpha^{\rm el}_{\rm obs}(1)$, $\Delta\alpha^{\rm el}_{\rm obs}$, for the above systems are also shown in Table I.

The values of $\alpha^{\rm el}_{\rm obs}(0)$, $\alpha^{\rm el}_{\rm obs}(1)$ and $\Delta\alpha^{\rm bl}_{\rm obs}$ are plotted against the dielectric constants ε_2 of the polar components, in Figs. 2—4.

As is seen from the above figures, it is likely that $\alpha^{\rm el}_{\rm obs}(1)$, $\alpha^{\rm el}_{\rm obs}(0)$ and $\Delta\alpha^{\rm el}_{\rm obs}$ have a kind of correlation to the dielectric constants of the polar components, that is, each plot gives approximately a straight line which intersects the abscissa at about $\varepsilon_2=2$. It should be noted, however, that a slight deviation is observed for butylcyanide and nitrobenzene which have much larger dipole moments than the others. The fact that the straight line intersects the absissa at about $\varepsilon_2=2$, which is neary equal to the dielectric constant of the non-polar components shows that on mixing these non-polar liquids with liquids having a dielectric constant of about 2, which might be non-polar, the electrostatic part of the heat of mixing vanishes.

This indicates that the estimation of $\alpha^{\rm n-el}$ mensioned above was not so inappropriate.

For *cis*-dichloroethylene—*trans*-dichloroethylene and pyridine—dioxane systems the plots

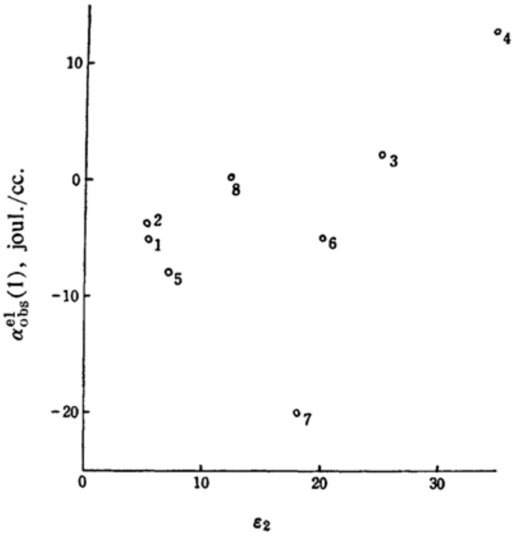

Fig. 5.

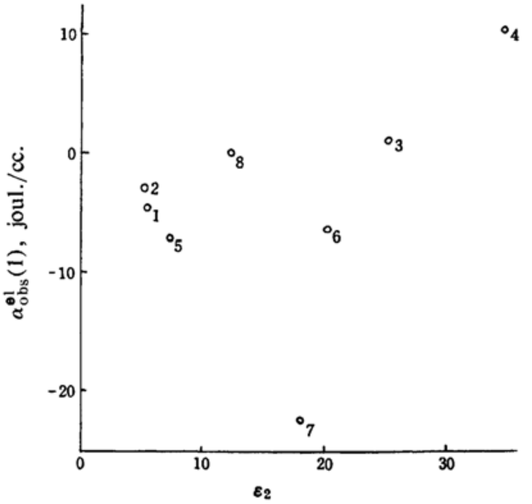

Fig. 6.

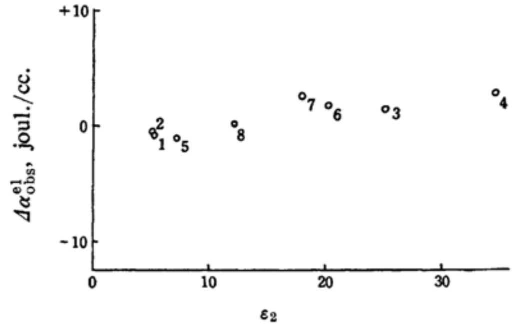

Fig. 7.

Figs. 5, 6, 7. The plots of observed values of electrostatic part of van Laar cofficients at concentrations $v_2=0$ and $v_2=1$ and their difference, $\alpha^{el}_{obs}(0)$, $\alpha^{el}_{obs}(1)$ and $\Delta\alpha^{el}_{obs}$ respectively vs. dielectric constant of polar components ε_2 for systems with aromatic non-polar components.

1. Chlorobenzene—Toluene
2. Bromobenzene—Toluene
3. Benzonitrile—Toluene
4. Nitrobenzene—Toluene
5. *n*-Butylchloride—Toluene
6. *n*-Butylcyanide—Toluene
7. Cyclohexanone—Toluene
8. Pyridine—Benzene

of $\alpha^{el}_{obs}(1)$, $\alpha^{el}_{obs}(0)$ and $\Delta\alpha^{el}_{obs}$ versus ε_2 deviate largely from the other systems. This might be due to the quadrupole moment of the non-polar component molecules. These non-polar molecules behave apparently as non-polar so far as the dielectric constant is concerned, but energetically not. The contribution from the local dipoles of these molecules which is not considered here, should be introduced, in systems containing molecules with quadrupole moment. The assumption of a single point dipole is drastic for the *cis*-dichloroethylene molecule, which has two large bond dipoles at a finite distance, and this may also be one of the reasons of the deviations for the system of *cis*- and *trans*-dichloroethylenes. For the pyridine—dioxane system the deviation is much greater than the above system, and this may be attributed to the large quadrupole moments of dioxane or the special interaction between pyridine and dioxane.

For the nitrobenzene—cyclohexane system, the plot of α^{el}_{obs} versus v_2 has a peculiar shape compared with the remaining systems of this group. This may be attributed to the antiparallel orientation of nitrobenzene molecules in pure liquid and its concentrated solution, which is evidenced by the increase of the dielectric constant on application of a strong electric field[4]. This antiparallel orientation exists only at a concentration higher than about 80 mol. %, and at a lower concentration antiparallel orientation vanishes. As the antiparallel orientation of dipoles in pure liquid and concentrated solution is stable, the vanishing of the antiparallel orientation requires some energy and this contributes to make the values of α^{el} increase. This effect is important in a concentration higher than 80 mol. %, and in the actual system the values of α are rather shifted in the positive direction in this concentration range compared with the other systems.

For systems in which non-polar components are aromatic such as toluene and benzene, the values of $\alpha^{el}_{obs}(1)$ and $\alpha^{el}_{obs}(0)$ and their differences $\Delta\alpha^{el}_{obs}$ are obtained by graphical extrapolation, and are shown in Table II.

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[4] A. Piekara, Achelekowski, *J. Chem. Phys.*, **25**, 794 (1956).

TABLE II. VALUES OF $\alpha^{\mathrm{el}}_{\mathrm{obs}}(0)$, $\alpha^{\mathrm{el}}_{\mathrm{obs}}(1)$ and $\Delta\alpha^{\mathrm{el}}_{\mathrm{obs}}$ IN joul./cc. FOR THE SYSTEMS IN WHICH NON-POLAR COMPONENTS ARE AROMATIC

System	$\alpha^{\mathrm{el}}_{\mathrm{obs}}(0)$	$\alpha^{\mathrm{el}}_{\mathrm{obs}}(1)$	$\Delta\alpha^{\mathrm{el}}_{\mathrm{obs}}$
Chlorobenzene—Toluene	−5.1	−4.3	−0.8
Bromobenzene—Toluene	−3.7	−3.1	−0.6
Benzonitrile—Toluene	2.5	1.1	1.4
Nitrobenzene—Toluene	13.2	10.5	2.7
n-Butylchloride—Toluene	−8.1	−7.2	−0.9
n-Butylcyanide—Toluene	−4.7	−6.5	1.8
Cyclohexanone—Toluene	−20.0	−22.5	2.5
Pyridine—Benzene	0.3	0	0.3

The values of $\alpha^{\mathrm{el}}_{\mathrm{obs}}(1)$, $\alpha^{\mathrm{el}}_{\mathrm{obs}}(0)$ and $\Delta\alpha^{\mathrm{el}}_{\mathrm{obs}}=\alpha^{\mathrm{el}}_{\mathrm{obs}}(0)-\alpha^{\mathrm{el}}_{\mathrm{obs}}(1)$ are plotted against the dielectric constant of the polar components and are shown in Figs. 5—7.

It is seen from the figures that no regulality is observed for $\alpha^{\mathrm{el}}_{\mathrm{obs}}(1)$ and $\alpha^{\mathrm{el}}_{\mathrm{obs}}(0)$ but for $\Delta\alpha^{\mathrm{el}}_{\mathrm{obs}}$ and they are nearly independent of the dielectric constants of the polar component. These are not on a line intersecting the abscissa at about $\varepsilon_2=2$.

Now the observed value will be compared with the calculated value. In Figs. 1.1—1.11, the values of $\alpha^{\mathrm{el}}_{\mathrm{calcd}}$ together with $\alpha^{\mathrm{el}}_{\mathrm{obs}}$ are plotted against the volume fractions of the polar component for the 21 binary systems of polar and non-polar liquids.

It is seen from the figures that for the systems in which non-polar components are non-aromatic both $\alpha^{\mathrm{el}}_{\mathrm{obs}}$ and $\alpha^{\mathrm{el}}_{\mathrm{calcd}}$ are positive and increase as the volume fraction of the polar component v_2 decreases. This confirms the fact that the variations of α with concentration are essentially due to the dipole of the polar component. However, quantitative agreements are poor for some of systems. For those in which non-polar components are aromatic, then differ in the manner of the change of α with concentration and sometimes even in their signs giving no qualitative agreement. This also confirms the fact that for the latter group of the systems, some kind of effect coherent to the aromaticity of the non-polar component which is not taken into consideration in the assumption of the derivation of the theory, occurs in the actual cases, and this may be the reason for the qualitative disagreement.

Further, quantitative comparison of $\alpha^{\mathrm{el}}_{\mathrm{obs}}$ and $\alpha^{\mathrm{el}}_{\mathrm{obs}}$ for the systems in which non-polar components are non-aromatic are made for the former group of the systems whose α^{el} may be considered to be explained principally by dipolar forces. The ratios of the calculated value to the experimental one, $\alpha^{\mathrm{el}}_{\mathrm{calcd}}/\alpha^{\mathrm{el}}_{\mathrm{obs}}$ are calculated for those systems at five values of concentration $v_2=1.00$, 0.75, 0.50, 0.25 and 0. The values of these ratios are plotted against the volume fraction in Fig. 8.

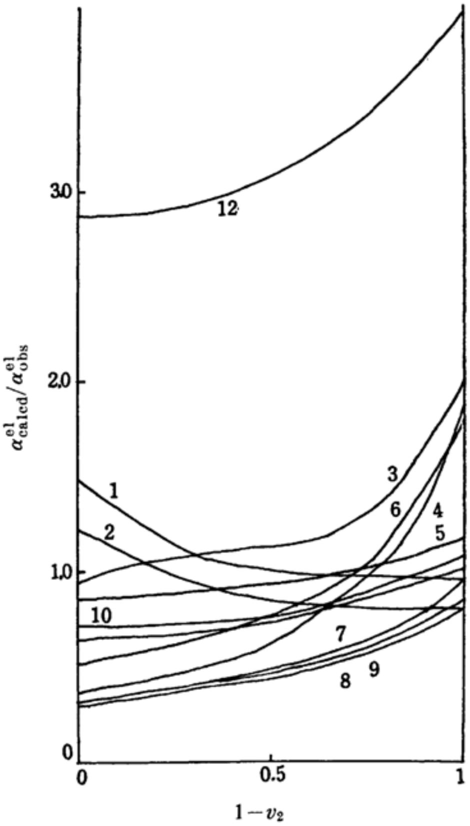

Fig. 8. Ratio $\alpha^{\mathrm{el}}_{\mathrm{calcd}}/\alpha^{\mathrm{el}}_{\mathrm{obs}}$ vs. volume fraction.

1. Chlorobenzene—Cyclohexane
2. Bromobenzene—Cyclohexane
3. Benzonitrile—Cyclohexane
4. Nitrobenzene—Cyclohexane
5. *n*-Butylchloride—Cyclohexane
6. *n*-Butylcyanide—Cyclohexane
7. Cyclohexanone—Cyclohexane
8. Diethylketone—Cyclohexane
9. Methylpropylketone—Cyclohexane
10. Chlorocyclohexane—Methylcyclohexane
11. Bromocyclohexane—Methylcyclohexane
12. *cis*-Dichloroethylene—*trans*-Dichloroethylene

It is seen from the result that most of the values of $\alpha^{\mathrm{el}}_{\mathrm{calcd}}/\alpha^{\mathrm{el}}_{\mathrm{obs}}$ are less than 2, whereas for the two systems, namely, of *cis*- and *trans*-dichloroethylene and of pyridine—dioxane, they differ considerably from the rest. Especially for the latter, it is too large to show in the figure. This indicates that the contribution due to the effect which cannot be explained merely with dipolar forces, presumably due to the quadrupole of the constituent molecules, is contained in the above two systems.

It indicates that in calculating electrostatic energy, contributions from multipoles higher than dipole such as quadrupole etc. must be taken into account for such systems.

It also indicates that for the rest of the group of the systems except the system containing the component molecules with larger dipole moments, such as nitrobenzene, benzonitrile and butylcyanide, the heats of mixing at infinite dilution of polar liquid in non-polar liquid are rather in good agreement with the theory despite of its rough assumptions. Rather good agreement obtained in a very dilute region for the systems with polar molecules of moderate magnitude of dipole moment, may be evidence that in these dilute regions, the assumptions made in the theory are not far from the actual circumstances.

Disagreement in the concentrated region may principally be due to the roughness of the theory such as the neglect of the short range interaction.

For systems containing polar molecules of large dipole moment the calculated values differ greatly from the experimental values.

This suggests that the larger the dipole moments is, the less satisfied is the condition of the assumption made in the theory in the actual circumstances.

Summary

The electrostatic part of the van Laar coefficients were derived from the observed value of heats of mixing and some regularity was found between these values and the dielectric constant of polar components if non-polar components are non-aromatic (group I). However, no regularity exists between them if non-polar components are aromatic (group II). These values were also compared with the calculated values. For group I, qualitative agreements were obtained and this confirms the fact that the variation of α with concentration is due to dipolar interaction of the polar components. The agreement is poor for systems containing a polar component with large dipole moments or for one containing a non-polar component with quadrupole moment. For group II, no qualitative agreement was obtained.

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