Thermodynamical Studies on Binary Systems Consisting of Polar and Non-polar Liquids. V. The Anomalies in the Binary Systems of Polar Liquid with Aromatic Non-polar Liquid

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(Received March 30, 1961)

In a previous paper it has been shown that an anomalous stabilization effect exists in those systems consisting of polar and aromatic non-polar components. To elucidate the cause of these phenomena, plausible explanations are proposed from the molecular view point.

Experimental Evaluation of the Anomalous Stabilization Effect

As is stated above, the binary systems containing the aromatic non-polar molecule and polar molecule show anomalous behavior in the heats of mixing.

First the decrease of the van Laar coefficient α due to the anomalous effect which was observed in aromatic non-polar solvents but not in non-aromatic solvents, will be estimated on reasonable assumptions.

Consider an imaginary non-polar liquid which is normal in nature such as cyclohexane, and its dielectric constant is the same as that of toluene. It may be reasonable to assume that the electrostatic part of the imaginary heat of mixing of the above imaginary non-polar liquid with polar liquids, if observed, would deviate from the theoretical values calculated for systems containing toluene in a previous paper, to the same extent as that of the deviation of the experimental value from the calculated one in the corresponding systems consisting of the same polar liquid and cyclohexane, because the dielectric constant of toluene and cyclohexane differs only slightly. Then the van Laar coefficient due to the electrostatic part of imaginary heat of mixing may be estimated according to the following expression by the use of $\alpha^{el}_{c.obs}$ and $\alpha^{el}_{c.calcd}$ for the cyclohexane-polar liquid system and the $\alpha^{el}_{t.calcd}$ for the toluene-polar liquid system.

$$\alpha^{el}_{t.obs}=\alpha^{el}_{c.obs}\cdot\alpha^{el}_{t.calcd}/\alpha^{el}_{c.calcd} \qquad (1)$$

where $\alpha^{el}_{t.obs}$ is the van Laar coefficient for an imaginary binary system mentioned above. The results obtained are shown in Table I.

TABLE I. VAN LAAR COEFFICIENT DUE TO STABILIZATION ENERGY α_{stab} AND THE VALUES OF STABILIZATION ENERGY ΔE_{stab} IN THE SYSTEMS COMPOSED OF POLAR LIQUID AND TOLUENE

System	v_2	α^{el}_1 joul./cc.	$\alpha_{stab}=\alpha^{el}_{obs}-\alpha^{el}_1$ joul./cc.	ΔE_{stab} joul./mol.
	1.0	4.16	− 8.5	0
Chlorobenzene —Toluene	0.75	5.76	−10.1	196
	0.50	7.18	−12.1	319
	0.25	8.57	−13.6	269
	0	10.07	−15.2	0
	1.0	5.54	− 8.6	0
Bromobenzene —Toluene	0.75	7.73	−11.0	218
	0.50	9.59	−13.1	348
	0.25	11.37	−15.0	299
	0	12.28	−16.0	0
	1.0	23.07	−22.0	0
Benzonitrile —Toluene	0.75	24.44	−23.9	467
	0.50	30.88	−30.9	812
	0.25	42.52	−42.3	840
	0	55.87	−53.4	0
	1.0	33.60	−23.1	0
Nitrobenzene —Toluene	0.75	37.00	−27.4	533
	0.50	37.63	−29.1	762
	0.25	44.13	−36.2	718
	0	64.95	−51.8	0
	1.0	9.95	−17.3	0
n-Butylchloride —Toluene	0.75	11.60	−19.4	384
	0.50	13.64	−21.3	565
	0.25	15.75	−24.5	488
	0	18.20	−26.9	0
	1.0	32.29	−38.8	0
n-Butylcyanide —Toluene	0.75	33.45	−40.6	808
	0.50	37.54	−45.5	1210
	0.25	45.25	−53.4	1067
	0	50.26	−55.0	0
	1.0	28.92	−51.4	0
Cyclohexanone —Toluene	0.75	28.48	−51.0	1003
	0.50	32.34	−55.2	1456
	0.25	41.15	−64.6	1286
	0	46.61	−66.6	0

These values would be the corresponding electrostatic part of the van Laar coefficient for heats of mixing of toluene and the polar liquids if toluene were normal in nature as cyclohexane is, and do not show any anomalous behavior. The difference between such apparent values and the observed values may be considered to be the contribution from the anomalous effect. The part of the contribution of the anomalous effect to the van Laar coefficient α_{stab} thus obtained are also shown in the same table together with the stabilization energy per mole of the solution. It is seen that α_{stab} is dependent on the concentration.

The Origin of the Anomalous Stabilization Effect

The Anisotropy of the Aromatic Non-polar Molecules.—If an anisotropic non-polar molecule is placed in an electric field, it tends to orient its most polarizable axis to be parallel to the direction of the electric field. In a region near the polar molecule, a strong electric field is produced arouud it and hence aromatic molecules in this region would tend to orient their most polarizable axis along the direction of the electric field. Then the effective dielectric constant of this region increases somewhat more than the original macroscopic value, the extent of which depends on the anisotropy of the non-polar molecule and the magnitude of the dipole moment of the polar molecule.

The increase of the dielectric constant of the non-polar liquid makes the calculated values of the van Laar coefficient decrease as is seen from the above results that the calculated values of the electrostatic part of the van Laar coefficient α^{el}_{calcd} for tolune-polar liquid system is an amount of 80∼90% of those for the corresponding system of cyclohexane-polar liquid. Anisotropy constants for benzene and toluene are reproduced for reference from the literature:

$$\text{for benzene}\begin{cases}\alpha_1=123.1\\ \alpha_2=123.1\\ \alpha_3=\ 63.5\end{cases}\quad \bar{\alpha}=103.2\quad \frac{\alpha_1}{\bar{\alpha}}=1.193$$

$$\text{for toluene}\begin{cases}\alpha_1=156.4\\ \alpha_2=136.6\\ \alpha_3=\ 74.8\end{cases}\quad \bar{\alpha}=122.6\quad \frac{\alpha_1}{\bar{\alpha}}=1.276$$

If we suppose that the non-polar molecules given above orient their most polarizable axis completely along the direction of the electric field produced by the polar molecule, the effective dielectric constant may be increased from 2.366 of toluene to about 3.

The values calculated with the values of 3 for the dielectric constant of non-polar liquid indicate the maximum contribution of this effect. In actual cases, however, the orientation of the non-polar molecule along the direction of the electric field is disturbed by thermal agitation and the effective dielectric constant may be less than 3.

The orientational effect in the solution consisting of anisotropic non-polar molecules accompanying the increase of effective dielectric constant in the region of small x_2 would make the values of $\alpha^{\text{el}}_{\text{calcd}}$ smaller than before.

But with this consideration alone it is impossible to make the values of α^{el} negative and also to explain the concentration dependence of α_{stab}.

The Addition Stabilizing Effect due to Orientation of Anisotropic Non-polar Molecules in an Electric Field.—The molecules of toluene and benzene are somewhat anisotropic, and when they are placed in a strong electric field, they tend to orient their most polarizable axis in the direction of the applied electric field. In the gaseous state this effect results in the increase of polarizability, and hence somewhat stabilizes the molecules. But this effect makes little contribution as was explained above.

In the liquid state, however, molecules interact with each other, and if we are admitted to assume the orientation of these molecules increases the intermolecular interaction energy, these stabilizing effects may be explained consistently.

Anisotropic non-polar molecules near a polar molecule are in a more ordered state than those far from the polar molecule because of the strong dipolar field of the latter. It may be reasonable to assume that in a region near the dipolar molecule, anisotropic non-polar molecules stick together more or less as they do in their solid state and the degree or the extent of the orientation depends on the magnitude of the dipolar field.

Let us consider an anisotropic non-polar molecule whose polarizabilities along three principal axes x, y and z are α_{x}, α_{y} and α_{z} respectively.

When this molecule is placed in an electric field F, then the electrostatic energy of the molecule, E is expressed as

$$E=-\frac{1}{2}(\alpha_{\text{x}}\cos^2\theta_{\mu\text{x}}+\alpha_{\text{y}}\cos^2\theta_{\mu\text{y}}+\alpha_{\text{z}}\cos^2\theta_{\mu\text{z}})F^2 \tag{2}$$

where $\theta_{\mu\text{x}}$, $\theta_{\mu\text{y}}$ and $\theta_{\mu\text{z}}$ denote the angles between the direction of the electric field and each principal x, y and z axis respectively.

For simplicity, assuming that

$$\alpha_{\text{x}}=\alpha_{\text{y}} \tag{3}$$

the electrostatic energy E is given by

$$\begin{aligned}E&=-\frac{1}{2}(\alpha_{\text{z}}\cos^2\theta_{\mu\text{z}}+\alpha_{\text{x}}\sin^2\theta_{\mu\text{z}})F^2\\&=-\frac{1}{2}\{(\alpha_{\text{z}}-\alpha_{\text{x}})\cos^2\theta_{\mu\text{z}}+\alpha_{\text{x}}\}F^2\end{aligned} \tag{4}$$

then

$$\begin{aligned}\overline{\cos^2\theta_{\mu z}}&=\frac{2\int_{\pi/2}^{0}\int_{0}^{2\pi}\cos^2\theta_{\mu\text{z}}\cdot\exp\left[\frac{1}{2}\{(\alpha_{\text{z}}-\alpha_{\text{x}})\cos^2\theta_{\mu\text{z}}+\alpha_{\text{x}}\}\times(F^2/\boldsymbol{k}T)\right]\cdot\sin\theta_{\mu\text{z}}\mathrm{d}\theta_{\mu\text{z}}\mathrm{d}\varphi}{\int_{\pi/2}^{0}\int_{0}^{2\pi}\exp\left[\frac{1}{2}\{\alpha_{\text{z}}-\alpha_{\text{x}})\cos^2\theta_{\mu\text{z}}+\alpha_{\text{x}}\}\times(F^2/\boldsymbol{k}T)\right]\cdot\sin\theta_{\mu\text{z}}\mathrm{d}\theta_{\mu\text{z}}\mathrm{d}\varphi}\\&=\frac{\int_{\pi/2}^{0}\cos^2\theta_{\mu\text{z}}\exp\left[\frac{1}{2}(\alpha_{\text{z}}-\alpha_{\text{x}})(F^2\cos^2\theta_{\mu\text{z}}/\boldsymbol{k}T)\right]\times\sin\theta_{\mu\text{z}}\mathrm{d}\theta_{\mu\text{z}}}{\int_{\pi/2}^{0}\exp\left[\frac{1}{2}(\alpha_{\text{z}}-\alpha_{\text{x}})F^2\cos^2\theta_{\mu\text{z}}/\boldsymbol{k}T\right]\cdot\sin\theta_{\mu\text{z}}\mathrm{d}\theta_{\mu\text{z}}}\end{aligned} \tag{5}$$

Putting $\cos^2\theta_{\mu\text{z}}=\text{x}$, and $1/2\cdot(\alpha_{\text{z}}-\alpha_{\text{x}})F^2/\boldsymbol{k}T=\boldsymbol{a}$, then the above expression becomes

$$\overline{x^2}=\frac{\int_0^1 x^2\mathrm{e}^{ax^2}\mathrm{d}x}{\int_0^1\mathrm{e}^{ax^2}\mathrm{d}x}=\frac{\left[\frac{x}{2a}\mathrm{e}^{ax^2}\right]_0^1}{\int_0^1\mathrm{e}^{ax^2}\mathrm{d}x}-\frac{1}{2a} \tag{6}$$

As the integration in the denominater, $\int\mathrm{e}^{ax^2}\mathrm{d}x$ can not be expressed in a simple formula, the integrand is expanded in a power series, and is integrated, and then the following expression is obtained

$$\begin{aligned}\int\mathrm{e}^{ax^2}\mathrm{d}x&=\int\left(1+ax^2+\frac{a^2x^4}{2\,!}+\frac{a^3x^6}{3\,!}+\cdots\right)\mathrm{d}x\\&=x+\frac{a}{3}x^3+\frac{a^2x^5}{5\cdot2\,!}+\frac{a^3x^7}{7\cdot3\,!}+\cdots\end{aligned} \tag{7}$$

For extreme cases of $a\ll1$ and $a\gg1$, the following approximate formula are obtained. For $a\ll1$

$$\int_0^1\mathrm{e}^{ax^2}\mathrm{d}x=1+\frac{a}{3}+\frac{a^2}{10}+\cdots \tag{8}$$

$$\left[\frac{x}{2a}\mathrm{e}^{ax^2}\right]_0^1=\frac{1}{2a}+\frac{1}{2}+\frac{a}{4}+\cdots \tag{9}$$

then

$$\begin{aligned}\frac{\left[\frac{x}{2a}\mathrm{e}^{ax^2}\right]_0^1}{\int_0^1\mathrm{e}^{ax^2}\mathrm{d}x}&=\left(\frac{1}{2a}+\frac{1}{2}+\frac{a}{4}+\cdots\right)\\&\quad\times\left(1+\frac{a}{3}+\frac{a^2}{10}+\cdots\right)^{-1}\\&=\frac{1}{2a}+\frac{1}{3}+\frac{7}{90}a+\cdots\end{aligned} \tag{10}$$

Then

$$\overline{\cos^2\theta_{\mu\text{z}}}=\frac{1}{3}+\frac{7}{90}a+\cdots \tag{11}$$

For $a \gg 1$, $\overline{\cos^2\theta_{\mu z}}$ tend to unity.

For the molecule with $\alpha_z > \alpha_x = \alpha_y$, $\overline{\cos^2\theta_{\mu z}}$ tends to 1/3 as a approaches to zero, and to 1 as it approaches to infinite. For the molecule $\alpha_z < \alpha_y = \alpha_y$, $\overline{\cos^2\theta_{\mu z}}$ tends to 1/3 as a approaches to zero and to 0 as it approaches to infinite.

As the value of $\overline{\cos^2\theta_{\mu z}}$ varies with the order of the molecular arrangement, it may be reasonable to define an order parameter as

$$s = (\overline{\cos^2\theta_{\mu z}} - 1/3)/(1-1/3) \quad \text{for } \alpha_z > \alpha_x \quad (12)$$

and

$$s = (1/3 - \overline{\cos^2\theta_{\mu z}})/1/3 \quad \text{for } \alpha_z < \alpha_x \quad (13)$$

s is proportional to a for small values of a and tends to approach to 1 for large values of a like the Langevin function. It may reasonably be assumed that the stabilization energy due to orientation of the anisotropic non-polar molecules is proportional to s and as a result it may be saturated in a strong electric field corresponding to a great value of a.

Now, the order of magnitude of a for actual cases will be considered. For the values of $(\alpha_z - \alpha_x)$ the value $\approx 60 \times 10^{-25}$ cc. per molecule of toluene is taken, and for F, if the values of an electric field at a distance of 3Å from a point dipole of 1D is taken, the value of F is 3.7×10^4 e. s. u., there a for $T = 300°\text{K}$ becomes 0.05 for 1D, and 0.82 for 4D. For chlorobenzene a is about 0.15 and for nitrobenzene this value is about 0.8.

Now, let us consider the order of magnitude of this effect. Since this effect is cooperative with respect to an aromatic non-polar molecule, it is natural that the contribution from this effect vanishes in a limit at zero concentration of aromatic non-polar component. Then it may be resonable to attribute the concentration dependent part of α_{stab} to this effect.

At infinite dilution of polar liquids, this stabilization energy per mole of polar liquid is from about 700 to 3200 joul.

On the other hand, heats of fusion, which may be considered to be a measure of orientational energy for benzene and toluene are about 9840 joul. and 6620 joul. per mole, respectively. As one polar molecule is surrounded by several of the nearest neighboring non-polar molecules at infinite dilution, a slight extent of ordered state in the group of molecules is possible to introduce considerable stabilization energy to their systems. Therefore, the magnitude of the above values of stabilizing energy seems to be not unreasonable as the contribution from this effect.

The stabilization energy of toluene at an infinite dilution of the polar molecule caused by 1 mol. of polar molecule is plotted against μ^2 in Fig. 1.

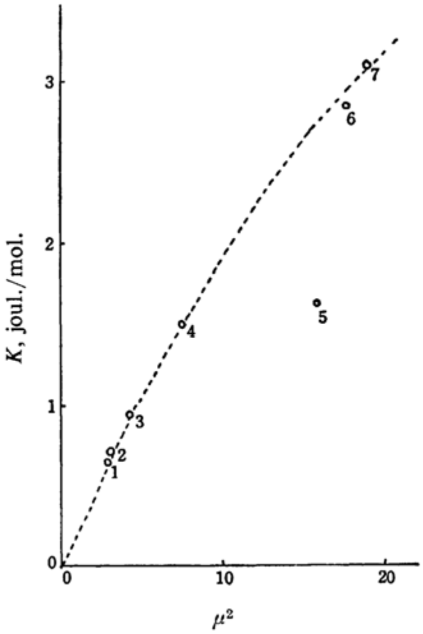

Fig. 1. Concentration dependent part of stabilization energy per mole of polar components at infinite dilution in toluene plotted against square of dipole moment of the polar molecules.

1. Chlorobenzene
2. Bromobenzene
3. *n*-Butylchloride
4. Cyclohexanone
5. *n*-Butylcyanide
6. Nitrobenzene
7. Benzonitrile

It is seen from the figure that the saturation effect is only slightly observed as the theory predicts. This fact makes the above explanation plausible. As for a concentration independent part of α_{stab}, further investigations will be necessary.

Summary

The anomalous stabilization energy for the systems containing polar and aromatic non-polar liquids was evaluated on reasonable assumptions. The van Laar coefficient due to this stabilizing effect was found to be dependent on the concentration. The stabilization effect corresponding to the concentration dependent part of the van Laar coefficient was explained by the cooperative orientation of aromatic non-polar molecules around the polar molecules.

The author wishes to express his thanks to Professor Ryoichi Fujishiro of Osaka City University and to Professor Yonezo Morino of the University of Tokyo for their constant encouragement and discussions.

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