Thermodynamical Studies on Binary Systems Consisting of Polar and Non-polar Liquids. III. Calculation of the Electrostatic Part of the Thermodynamic Excess Functions due only to the Dipole of the Polar Molecule for the Binary System Composed of Polar and Non-polar Liquids according to Onsager's Model

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In the previous paper it has been shown that in the systems containing non-aromatic non-polar components, the increase of van Laar coefficient with the decrease of the concentration of the polar component may be due to its dipole moment and that a kind of stabilizing effect exists in the systems containing aromatic non-polar components. In order to confirm the fact that such a variation of the van Laar coefficient with concentration in the former group of the systems is due to the dipoles of the polar components and to elucidate the cause of the stabilization effect in the latter group of the systems, theoretical formulas based on Onsager's model of polar liquids are derived to explain the electrostatic part of the excess thermodynamic quantities due only to the dipole of the polar component, by neglecting the effect of higher multipoles for a binary system of polar and non-polar liquids, and are applied to the actual systems for which the heats of mixing were measured.

Derivation of Theoretical Expressions

In deriving the expressions of the electrostatic part of the thermodynamic excess functions due only to the dipole of the polar component for a binary system of polar and non-polar liquids, the following assumptions are made according to Onsager[1]:

1) The polar molecules is spherical.

2) The dipole is a point dipole and is located at the center of the molecule.

3) The medium surrounding the polar molecule is a continuous one having macroscopic isotropic dielectric constant.

4) The polarizability of the polar molecule is isotropic.

Then further the following assumption is imposed:

5) There is no volume change on mixing.

If a molecule of dipole moment μ and of polarizability α is placed at a cavity of radius a in a medium of dielectric constant ε, the reaction field R due to the dielectric is

$$R=\mu\cdot g \tag{1}$$

where g is given by

$$g=\frac{2(\varepsilon-1)}{2\varepsilon+1-(2\alpha/a^3)(\varepsilon-1)}\cdot\frac{1}{a^3} \tag{2}$$

The electrostatic work w required for the formation of a dipole μ in the medium is given by

$$w=-1/2\cdot g\cdot\mu^2 \tag{3}$$

Then according to Barker[2], the electrostatic part of the free energy of mixing F^{Eel}, which is equal to G^{Eel} for a condensed system, for 1 mol. of a binary mixture in which the two components have the same molecular size and polarizability but different dipole moments μ_1 and μ_2, is given by

$$F^{\mathrm{Eel}}=G^{\mathrm{Eel}}=\frac{1}{2}N_{\mathrm{A}}({\mu^2}_1-{\mu^2}_2)\times\left(x_1\int_{x_1}^{1}g\mathrm{d}x_1-x_2\int_{0}^{x_1}g\mathrm{d}x_1\right) \tag{4}$$

where N_{A} is the Avogadro Number, x_1 and x_2 denote the mole fraction of the components 1 and 2 respectively. For a binary solution in which one component is polar and the other is non-polar, the electrostatic part of the free energy of mixing is given by

$$G^{\mathrm{Eel}}=\frac{1}{2}N_{\mathrm{A}}\mu^2\left\{x_2\int_{x_2}^{1}g\mathrm{d}x_1-(1-x_2)\int_{0}^{x_2}g\mathrm{d}x_2\right\} \tag{5}$$

where μ denotes the dipole moment of the polar molecule, and x_2 the mole fraction of the polar component in the solution.

Then other thermodynamic functions may be derived from the well-known thermodynamic relations:

$$H^{\mathrm{Eel}}=G^{\mathrm{Eel}}-T\cdot\frac{\partial G^{\mathrm{Eel}}}{\partial T}$$

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[1] L. Onsager, *J. Am. Chem. Soc.*, **58**, 1486 (1936).

[2] J. A. Barker, *Proc. Roy. Soc.*, **A219**, 367 (1953).

$$S^{\mathrm{Eel}}=-\frac{\partial G^{\mathrm{Eel}}}{\partial T}$$

and the following expressions are obtained.

$$H^{\mathrm{Eel}}=\frac{1}{2}N_{\mathrm{A}}\mu^2\left\{x_2\int_{x_2}^{1}h\mathrm{d}x_2-(1-x_2)\int_0^{x_2}h\mathrm{d}x_2\right\} \tag{6}$$

$$S^{\mathrm{Eel}}=\frac{1}{2}N_{\mathrm{A}}\mu^2\left\{x_2\int_{x_2}^{1}s\mathrm{d}x_2(1-x_2)\int_0^{x_2}s\mathrm{d}x_2\right\} \tag{7}$$

where

$$h=g-T\cdot\partial g/\partial T \tag{8}$$

and

$$s=-\partial g/\partial T \tag{9}$$

If the polarizability α of the polar molecule is expressed by

$$\frac{n_2{}^2-1}{n_2{}^2+2}=\frac{4}{3}\pi N\alpha \tag{10}$$

where N is the number of polar molecules in a unit volume of the pure liquid and n_2 is the refractive index of the polar liquid, and the molar volume of the polar molecule, V_{M} is taken as $4/3\cdot\pi N_{\mathrm{A}}a^3$. Then g is expressed as

$$g=\frac{8}{3}\pi\frac{1}{V_{\mathrm{M}}}\cdot N_{\mathrm{A}}\cdot\frac{\varepsilon(x_2)-1}{2\varepsilon(x_2)+n_2{}^2}\cdot\frac{n_2{}^2+2}{3} \tag{11}$$

For 1 mol. of solution the above quantities are given as follows.

$$G^{\mathrm{Eel}}=\frac{4}{3}\pi\frac{N_{\mathrm{A}}{}^2}{V_{\mathrm{M}}}\cdot\frac{n_2{}^2+2}{3}\mu^2 \times\left\{x_2\int_{x_2}^{1}\frac{\varepsilon(x_2)-1}{2\varepsilon(x_2)+n_2{}^2}\mathrm{d}x_2 -(1-x_2)\int_0^{x_2}\frac{\varepsilon(x_2)-1}{2\varepsilon(x_2)+n_2{}^2}\mathrm{d}x_2\right\} \tag{12}$$

$$H^{\mathrm{Eel}}=\frac{4}{3}\pi\frac{N_{\mathrm{A}}{}^2}{V_{\mathrm{M}}}\cdot\frac{n_2{}^2+2}{3}\mu^2 \times\left\{x_2\int_{x_2}^{1}\frac{\varepsilon(x_2-1)}{2\varepsilon(x_2)+n_2{}^2}(1-A(x_2)\cdot T)\mathrm{d}x_2 -(1-x_2)\int_0^{x_2}\frac{\varepsilon(x_2)-1}{2\varepsilon(x_2)+n_2{}^2} \times(1-A(x_2)\cdot T)\mathrm{d}x_2\right\} \tag{13}$$

$$S^{\mathrm{Eel}}=\frac{4}{3}\pi\frac{N_{\mathrm{A}}{}^2}{V_{\mathrm{M}}}\cdot\frac{n_2{}^2+2}{3}\mu^2 \times\left\{x_2\int_{x_2}^{1}\frac{\varepsilon(x_2)-1}{2\varepsilon(x_2)+n_2{}^2}A(x_2)\mathrm{d}x_2 -(1-x_2)\int_0^{x_2}\frac{\varepsilon(x_2)-1}{2\varepsilon(x_2)+n_2{}^2}A(x_2)\mathrm{d}x_2\right\} \tag{14}$$

where $A(x_2)$ is given by

$$A(x_2)=\frac{1}{V_{\mathrm{M}}}\frac{\mathrm{d}V_{\mathrm{M}}}{\mathrm{d}T} +\left(\frac{1}{\varepsilon(x_2)-1}-\frac{2}{2\varepsilon(x_2)+n_2{}^2}\right)\frac{\mathrm{d}\varepsilon(x_2)}{\mathrm{d}T} +\left(\frac{1}{n_2{}^2+2}-\frac{1}{2\varepsilon(x_2)+n_2{}^2}\right)2n_2\frac{\mathrm{d}n_2}{\mathrm{d}T} \tag{15}$$

which is easily derived by taking the logarithm of g and differentiating it with temperature. In the above expressions the following notations are used:

$\varepsilon(x_2)$: the dielectric constant of the solution in which the mole fraction of the polar component is x_2,

n_2: the refractive index of the polar liquid,

N_{A}: Avogadro's number,

V_{M}: the molar volume of the polar liquid, and

T: absolute temperature.

The Application of the Theory to the Actual Systems

The Necessary Data for the Calculation.—In applying the theory to the actual systems, it is necessary to have the numerical values of the following quantities:

1) the thermal expansion coefficient of the polar liquid,

2) the dielectric constant of the pure polar liquid, ε_2,

3) the temperature dependence of ε_2, $\mathrm{d}\varepsilon_2/\mathrm{d}T$,

4) the refractive index of the pure polar liquid, n_2,

5) the temperature dependence of n_2, $\mathrm{d}n_2/\mathrm{d}T$,

6) the density of the pure polar liquid, d,

7) the dipole moments of the polar component in vacuum, μ,

8) the dielectric constant of the solution, ε_{12}, and

9) the temperature dependence of ε_{12}, $\mathrm{d}\varepsilon_{12}/\mathrm{d}T$.

It is preferable to use the values of these constants which are determined experimentally, but unfortunately they are not available for all the systems considered in this experiment. In fact, for 1, 2, 4, 6 and 7 the values are available for all the components, but for 3 and 5 the values are only partly available and for 8 and 9 none of the values are available for all the systems. For those which are not available in the literature, they are derived from the relevant values on reasonable assumptions or the experimental rules as described in the following.

The Derivation of the Values of the Quantities which are not Available in the Literature.—(1) The temperature dependence of the dielectric constant of the polar liquid. According to Onsager, the dielectric constant of a

TABLE I. PHYSICAL CONSTANTS OF THE COMPONENTS USED FOR THE CALCULATION

Substance	Therm.exp. coeff., $\times 10^3$ per °C	Dielectric const., ε	Refractive index for Na D line n_D	Temp. dependence of $\varepsilon \times 10^2$ per °C	Temp. dependence of $n_D \times 10^4$ per °C	Molecular volume cc.	Dipole moment Debye unit
Chlorobenzene	0.981	5.612	1.52211	−1.6	−5.4	101.74	1.70
Bromobenzene	0.887	5.40	1.55762	−1.76*	−4.9	105.51	1.74
Benzonitrile	0.88	25.2	1.5265	−8.7	−3.4	103.50	4.39
Nitrobenzene	0.824	34.89	1.55057	−18.6	−4.0	103.16	4.21
Diethyl ketone	1.203	17.00	1.39003	−8.43*	−4.7	106.40	2.71
Methyl propyl ketone	1.203	17.00	1.39003	−8.43*	−4.7	106.40	2.71
n-Butylchloride	1.25	7.39	1.39954	−3.24*	−5.0	105.73	2.07
n-Butylcyanide	1.15	20.3	1.38170	−8.87*	−4.3	105.15	4.09
Cyclohexanone	0.947	18.3	1.44941	−8.58*	−4.9	104.67	2.75
Chlorocyclohexane	0.949	7.906**	1.46555	−3.28*	−5.1	119.37	2.07
Bromocyclohexane	0.891	7.945**	1.5020	−3.23*	−5.2	124.43	2.15
Pyridine	1.029	12.3	1.5067	−5.59	−5.0	81.31	2.22
cis-Dichloroethylene	1.288	9.0	1.44903	−4.45*	−6.5	76.17	1.80
trans-Dichloroethylene	1.67	2.14	1.4405	−0.263*	−10.1	77.28	0
Methylcyclohexane	1.13	2.020	1.42058	−0.16	−5.1	128.38	0
Cyclohexane	1.197	2.0199	1.42353	−0.16	−5.4	108.09	0
Toluene	1.109	2.3661	1.49413	−0.24	−5.6	106.85	0(0.37)
Benzene	1.197	2.284	1.49790	−0.20	−6.4	89.40	0
1,4-Dioxane	1.34	2.209	1.42025	−0.226*	−4.3	85.80	0

* Calculated according to the formula 16.

** Kindly measured by Mrs. K. Sasaki of this Institute.

TABLE II. THE CALCULATED VALUES OF THE ELECTROSTATIC PART OF THERMODYNAMIC EXCESS FUNCTIONS FOR BINARY SYSTEMS CONTAINING POLAR AND NON-AROMATIC NON-POLAR COMPONENTS

System	x_2	$G^{\mathrm{Eel}}_{\mathrm{calcd}}$	$H^{\mathrm{Eel}}_{\mathrm{calcd}}$	$TS^{\mathrm{Eel}}_{\mathrm{calcd}}$
Chlorobenzene —Cyclohexane	1.000	0	0	0
	0.916	36.8	58.4	21.6
	0.829	70.2	112.6	42.4
	0.743	97.3	158.4	61.6
	0.653	119.0	196.7	77.7
	0.559	133.6	224.7	91.1
	0.462	139.2	239.2	100.0
	0.360	133.5	234.9	101.4
	0.251	113.2	203.0	89.9
	0.132	72.1	131.8	59.7
	0	0	0	0
Bromobenzene —Cyclohexane	1.000	0	0	0
	0.914	38.7	62.5	23.8
	0.827	72.7	118.9	46.2
	0.738	101.7	168.2	66.5
	0.647	123.9	208.5	84.6
	0.553	138.5	237.3	98.8
	0.456	144.0	251.3	107.3
	0.354	137.9	245.2	107.3
	0.246	111.5	211.8	100.3
	0.130	70.3	137.5	67.2
	0	0	0	0
Benzonitrile —Cyclohexane	1.000	0	0	0
	0.908	234.3	216.6	−17.7
	0.816	452.4	426.4	−26.0
	0.722	652.8	626.2	−26.6
	0.628	829.2	812.2	−17.0
	0.532	974.0	978.6	4.6
	0.435	1073.4	1113.9	40.5
	0.337	1107.3	1199.0	91.7
	0.231	1032.7	1189.0	156.9
	0.129	823.5	1015.8	192.3
	0.070	541.3	713.5	172.2
	0	0	0	0
Nitrobenzene —Cyclohexane	1.000	0	0	0
	0.908	199.9	130.3	−69.6
	0.814	389.8	262.0	−127.8
	0.720	566.0	394.4	−171.6
	0.625	725.0	527.6	−197.4
	0.529	859.2	658.9	−200.3
	0.431	959.4	788.7	−170.7
	0.333	1007.6	902.4	−105.2
	0.232	970.2	977.3	7.1
	0.127	777.1	913.5	136.4
	0.069	519.6	719.6	200.0
	0	0	0	0

TABLE II. (Continued)

System	x_2	$G^{\mathrm{Eel}}_{\mathrm{calcd}}$	$H^{\mathrm{Eel}}_{\mathrm{calcd}}$	$TS^{\mathrm{Eel}}_{\mathrm{calcd}}$
n-Butylchloride —Cyclohexane	1.000	0	0	0
	0.910	59.9	89.2	29.3
	0.819	113.2	178.6	65.4
	0.727	158.6	259.8	101.2
	0.633	194.7	326.6	131.9
	0.538	219.9	378.9	159.0
	0.440	230.8	411.3	180.5
	0.340	223.4	414.3	190.9
	0.236	191.5	371.9	180.4
	0.124	124.0	254.3	130.3
	0	0	0	0
Diethyl ketone (Methyl propyl ketone) —Cyclohexane	1.000	0	0	0
	0.906	85.9	87.2	1.3
	0.811	165.3	171.9	6.6
	0.716	236.3	252.6	16.3
	0.620	296.9	327.6	30.7
	0.524	344.1	384.2	40.1
	0.427	373.4	448.1	74.7
	0.328	377.7	489.9	112.2
	0.227	343.9	470.9	127.0
	0.121	244.6	369.7	125.1
	0.064	152.1	246.9	94.8
	0	0	0	0
Cyclohexanone —Cyclohexane	1.000	0	0	0
	0.902	104.0	99.2	−4.8
	0.809	194.7	190.0	−4.7
	0.715	276.4	277.1	0.7
	0.620	346.6	358.8	12.2
	0.525	401.9	432.1	30.2
	0.428	436.8	491.7	54.9
	0.329	442.7	527.8	85.1
	0.227	403.7	518.4	114.7
	0.119	283.5	403.2	119.7
	0.060	169.1	258.8	89.7
	0	0	0	0
n-Butylcyanide —Cyclohexane	1.000	0	0	0
	0.906	185.4	170.2	−15.2
	0.812	358.1	336.9	−21.2
	0.717	514.2	497.3	−16.9
	0.621	649.8	648.9	−0.9
	0.524	757.5	786.0	28.5
	0.427	828.3	901.6	73.3
	0.328	845.8	977.5	131.7
	0.227	780.3	976.1	195.8
	0.121	565.4	789.0	223.6
	0.062	347.0	529.0	182.0
	0	0	0	0
Chlorocyclohexane —Methylcyclohexane	1.000	0	0	0
	0.915	49.5	69.9	20.4
	0.828	94.2	135.7	41.5
	0.740	133.2	196.4	63.2
	0.649	165.1	249.8	84.7
	0.555	188.0	292.9	104.9
	0.459	199.3	320.9	121.6
	0.358	195.3	326.6	131.3
	0.251	169.9	297.4	127.5
	0.134	112.2	208.1	95.9
	0	0	0	0
Bromocyclohexane —Methylcyclohexane	1.000	0	0	0
	0.912	53.9	75.5	21.6
	0.824	102.3	146.0	43.7
	0.734	144.0	210.1	66.1
	0.642	177.7	266.0	88.3
	0.548	201.5	310.6	109.1
	0.452	212.8	338.9	126.1
	0.352	207.8	343.5	135.7
	0.246	180.2	301.5	131.3
	0.131	118.8	216.8	98.0
	0	0	0	0
cis-Dichloroethylene —*trans*-Dichloroethylene	1.000	0	0	0
	0.908	64.1	103.5	39.4
	0.815	121.3	199.6	78.3
	0.727	166.9	280.6	113.7
	0.626	208.7	360.7	152.0
	0.529	240.5	419.4	178.9
	0.430	256.8	454.9	198.1
	0.328	247.5	456.6	209.1
	0.222	209.3	405.2	195.9
	0.107	126.5	260.2	133.7
	0	0	0	0
Pyridine —1,4-Dioxane	1.000	0	0	0
	0.913	91.5	107.0	15.5
	0.824	175.3	209.7	34.4
	0.734	249.9	306.3	56.4
	0.643	312.6	394.2	81.6
	0.550	360.9	470.2	109.3
	0.454	388.9	527.0	138.1
	0.356	389.9	554.2	164.3
	0.253	351.6	530.2	178.6
	0.141	251.0	408.6	157.6
	0	0	0	0

Table III. The calculated values of the electrostatic part of thermodynamic excess functions for binary systems containing polar and aromatic non-polar components

System	x_2	$G^{\mathrm{Eel}}_{\mathrm{calcd}}$	$H^{\mathrm{Eel}}_{\mathrm{calcd}}$	$TS^{\mathrm{Eel}}_{\mathrm{calcd}}$
Chlorobenzene —Toluene	1.000	0	0	0
	0.905	34.5	55·3	20.8
	0.806	64.6	105.1	40.5
	0.707	87.8	145.3	57.5
	0.613	103.4	173.5	70.1
	0.498	112.4	192.1	79.7
	0.386	110.2	192.0	81.8
	0.269	94.5	168.9	74.4
	0.143	61.2	111.9	50.7
	0.005	2.8	5.2	2.4
	0	0	0	0
Bromobenzene —Toluene	1.000	0	0	0
	0.902	36.4	64.2	27.8
	0.802	67.3	120.3	53.0
	0.700	92.2	166.5	74.3
	0.595	109.2	200.5	91.3
	0.488	117.3	218.9	101.6
	0.376	114.5	216.5	102.0
	0.248	98.0	185.9	87.9
	0.133	57.3	115.8	58.5
	0	0	0	0
Benzonitrile —Toluene	1.000	0	0	0
	0.906	224.9	204.8	−20.1
	0.810	434.4	401.4	−33.0
	0.714	624.8	587.8	−37.0
	0.618	789.7	759.2	−30.5
	0.519	922.1	910.0	−12.1
	0.421	1007.4	1026.9	19.5
	0.321	1025.7	1091.1	65.4
	0.214	932.6	1053.3	120.7
	0.109	648.6	794.4	145.8
	0.049	349.9	457.6	107.7
	0	0	0	0
Nitrobenzene —Toluene	1.000	0	0	0
	0.905	189.3	121.0	−68.3
	0.810	367.9	242.9	−125.0
	0.714	532.1	364.2	−167.9
	0.617	677.7	483.8	−193.9
	0.519	798.5	599.7	−198.8
	0.420	884.2	707.3	−176.9
	0.320	916.8	795.4	−121.4
	0.218	861.7	835.2	−26.5
	0.112	631.2	719.7	88.5
	0.054	377.9	491.0	113.1
	0	0	0	0
n-Butylchloride —Toluene	1.000	0	0	0
	0.901	56.1	86.4	30.3
	0.802	104.6	168.3	63.7
	0.701	144.5	240.2	95.7
	0.600	174.0	298.9	124.9
	0.496	191.4	339.5	148.1
	0.390	193.1	355.2	161.2
	0.281	174.6	334.7	160.1
	0.168	128.9	259.7	130.8
	0.046	43.8	92.8	49.0
	0	0	0	0
Cyclohexanone —Toluene	1.000	0	0	0
	0.908	89.0	84.8	−4.2
	0.802	181.9	178.1	−3.8
	0.705	257.1	258.8	1.7
	0.607	320.1	333.2	13.1
	0.508	367.5	397.9	30.4
	0.409	393.8	447.3	53.5
	0.307	390.0	470.5	80.5
	0.203	339.8	443.3	103.5
	0.092	205.9	298.0	92.1
	0.031	81.7	126.9	45.2
	0	0	0	0
n-Butylcyanide —Toluene	1.000	0	0	0
	0.903	181.0	167.6	−13.4
	0.805	348.0	330.3	−17.7
	0.707	497.9	486.4	−11.5
	0.609	625.9	632.1	6.2
	0.510	725.5	762.2	36.7
	0.410	786.6	866.9	80.3
	0.309	792.9	928.0	135.1
	0.205	714.1	903.4	189.1
	0.098	482.8	674.5	191.7
	0.040	206.1	318.9	112.8
	0	0	0	0
Pyridine —Benzene	1.000	0	0	0
	0.914	88.7	107.0	18.3
	0.827	170.2	210.0	39.8
	0.738	243.3	308.4	65.1
	0.647	304.9	398.3	93.4
	0.553	352.3	475.5	123.2
	0.456	379.6	533.4	153.8
	0.356	379.5	559.6	180.1
	0.249	339.0	530.9	191.9
	0.134	233.5	394.9	161.4
	0	0	0	0

polar liquid ε_2 is related to temperature as

$$\varepsilon_2 - n_2^2 = \frac{3\varepsilon_2}{2\varepsilon_2 + n_2^2} \cdot \frac{(n_2^2+2)^2}{3} \cdot \frac{4\pi N}{3kT}\mu^2 \qquad (16)$$

By assuming that the dipole moment μ of the polar molecule is independent of temperature, we obtain the following expression, by taking the logarithm of both sides of the formula 16 and differentiating it with the temperature:

$$\left(\frac{1}{\varepsilon_2 - n_2^2} + \frac{2}{2\varepsilon_2 + n_2^2} - \frac{1}{\varepsilon_2}\right)\frac{\mathrm{d}\varepsilon_2}{\mathrm{d}T} + \left(\frac{1}{2\varepsilon_2 + n_2^2} - \frac{1}{\varepsilon_2 - n_2^2} - \frac{2}{n_2^2+2}\right)2n_2\frac{\mathrm{d}n_2}{\mathrm{d}T} = \frac{1}{N}\cdot\frac{\mathrm{d}N}{\mathrm{d}T} - \frac{1}{T} \qquad (17)$$

where $1/N\cdot\mathrm{d}N/\mathrm{d}T$ is the thermal expansion coefficient of the polar liquid reversed in sign. All the values in the above expression are available except $\mathrm{d}\varepsilon_2/\mathrm{d}T$. Then the values of $\mathrm{d}\varepsilon_2/\mathrm{d}T$ can be derived by the relevant values such as ε_2, n_2, $\mathrm{d}n_2/\mathrm{d}T$, T and the thermal expansion coefficient.

(2) The temperature dependence of the refractive index of the liquid. The refractive index n of a liquid can approximately be expressed as $(n^2-1)/(n^2+2)\cdot 1/\rho = \text{const.}$ where ρ is the density of the liquid. Differentiating it with temperature, we obtain

$$\frac{\mathrm{d}n}{\mathrm{d}T} = \frac{(n^2-1)(n^2+2)}{6n}\;\frac{1}{\rho}\;\frac{\mathrm{d}\rho}{\mathrm{d}T} \qquad (18)$$

$1/\rho\cdot\mathrm{d}\rho/\mathrm{d}T$ is the thermal expansion coefficient of the liquid reversed in sign. Then we can derive the values of $\mathrm{d}n/\mathrm{d}T$ from the refractive index and the thermal expansion coefficient of the liquid.

(3) The dielectric constant of the solution, ε_{12}. According to Onsager, the dielectric constant of a binary solution of polar and nonpolar liquid is expressed as

$$\frac{3(1-v_2)(\varepsilon_{12}-n_1^2)\varepsilon_{12}}{2\varepsilon_{12}+n_1^2} + \frac{3v_2(\varepsilon_{12}-n_2^2)}{2\varepsilon_{12}+n_2^2} = \frac{4\pi N v_2 \mu^2}{3kT}\left\{\frac{\varepsilon_{12}(n_2^2+2)}{2\varepsilon_{12}+n_2^2}\right\}^2 \qquad (19)$$

where v_2 is the volume fraction of the polar components.

By replacing μ^2 in the above expression with

$$\frac{9(\varepsilon_2-n_2^2)(2\varepsilon_2+n_2^2)kT}{\varepsilon_2(n_2^2+2)^2\cdot 4\pi N} = \mu^2 \qquad (20)$$

which is obtained from Onsager's expression of the dielectric constant for a pure polar liquid, we obtain[3]

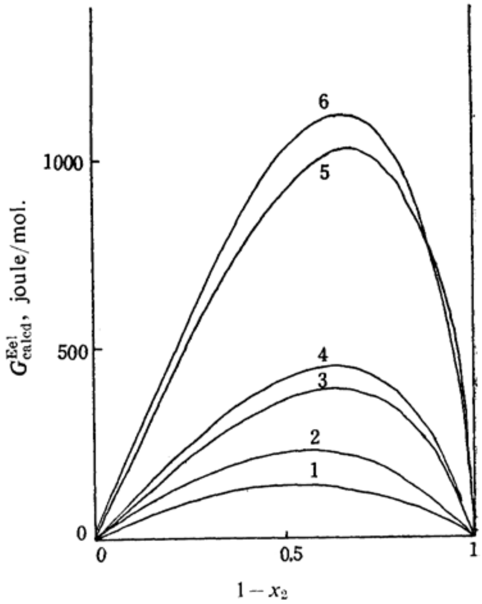

Fig. 1. $G^{\mathrm{Eel}}_{\mathrm{calcd}}$ vs. mol. fraction.

1. Chlorobenzene—Cyclohexane
2. *n*-Butylchloride—Cyclohexane
3. Diethyl ketone—Cyclohexane
4. Cyclohexanone—Cyclohexane
5. Nitrobenzene—Cyclohexane
6. Benzonitrile—Cyclohexane

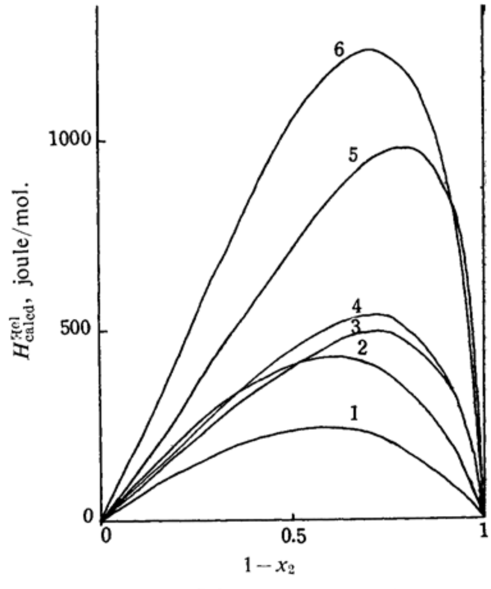

Fig. 2. $H^{\mathrm{Eel}}_{\mathrm{calcd}}$ vs. mol. fraction.

1. Chlorobenzene—Cyclohexane
2. *n*-Butylchloride—Cyclohexane
3. Diethyl ketone—Cyclohexane
4. Cyclohexanone—Cyclohexane
5. Nitrobenzene—Cyclohexane
6. Benzonitrile—Cyclohexane

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[3] T. Hanai, N. Koizumi and R. Gotō, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 17 (1959).

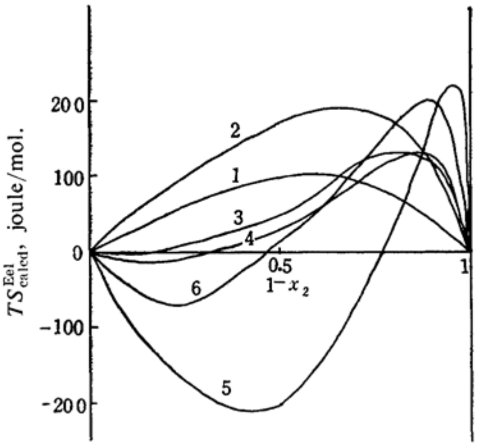

Fig. 3. $TS^{\mathrm{Eel}}_{\mathrm{calcd}}$ vs. mol. fraction.

1. Chlorobenzene—Cyclohexane
2. *n*-Butylchloride—Cyclohexane
3. Diethyl ketone—Cyclohexane
4. Cyclohexanone—Cyclohexane
5. Nitrobenzene—Cyclohexane
6. Benzonitrile—Cyclohexane

$$\frac{\varepsilon_{12}-\varepsilon_1}{2\varepsilon_{12}-n_1^2}\cdot(1-v_2)+\frac{(\varepsilon_{12}-\varepsilon_2)(2\varepsilon_{12}\varepsilon_2+n_2^4)}{\varepsilon_2(2\varepsilon_{12}+n_2^2)^2}v_2=0 \tag{21}$$

where ε_1 and n_1 are the dielectric constant and refractive index of the non-polar liquid respectively, other notation being the same as those already described. All the values in the above expression 21 are known except ε_{12} and v_1. The dielectric constant of the solution ε_{12} can be calculated from the expression 21 for any given values of concentration v_2.

(4) The temperature dependence of ε_{12}, $\mathrm{d}\varepsilon_{12}/\mathrm{d}T$. It is approximated by a weighted mean such as

$$\frac{\mathrm{d}\varepsilon_{12}}{\mathrm{d}T}=\frac{\varepsilon_2-\varepsilon_{12}}{\varepsilon_2-\varepsilon_1}\cdot\frac{\mathrm{d}\varepsilon_1}{\mathrm{d}T}+\frac{\varepsilon_{12}-\varepsilon_1}{\varepsilon_2-\varepsilon_1}\cdot\frac{\mathrm{d}\varepsilon_2}{\mathrm{d}T} \tag{22}$$

$\mathrm{d}\varepsilon_1/\mathrm{d}T$ is the temperature dependence of the dielectric constant of the non-polar liquid. If $\mathrm{d}\varepsilon_1/\mathrm{d}T$ is not available, it is derived by using the following expression

$$\frac{\varepsilon_1-1}{\varepsilon_1+2}\cdot\frac{1}{\rho}=\text{constant} \tag{23}$$

TABLE IV. THE ELECTROSTATIC PART OF VAN LAAR COEFFICIENTS, $\alpha^{\mathrm{el}}_{\mathrm{calcd}}$ CALCULATED ACCORDING TO ONSAGER'S MODEL FOR BINARY SYSTEMS CONSISTING OF POLAR AND NON-AROMATIC NON-POLAR MOLECULES

System	v_2	$\alpha^{\mathrm{el}}_{\mathrm{calcd}}$ joule/cc.	System	v_2	$\alpha^{\mathrm{el}}_{\mathrm{calcd}}$ joule/cc.
Chlorobenzene —Cyclohexane	1.000	7.18	Benzonitrile —Cyclohexane	1.000	23.21
	0.9115	7.07		0.9045	24.13
	0.8203	7.43		0.8089	26.44
	0.7312	7.80		0.7132	29.22
	0.6387	8.20		0.6173	32.68
	0.5441	8.67		0.5208	37.12
	0.4468	9.20		0.4244	42.98
	0.3460	9.81		0.3269	51.15
	0.2395	10.47		0.2236	64.03
	0.1256	11.19		0.1239	87.05
	0	12.03		0.0672	105.58
				0	131.96
Bromobenzene —Cyclohexane	1.000	7.28	Nitrobenzene —Cyclohexane	1.000	13.67
	0.9123	7.39		0.9036	14.45
	0.8235	7.72		0.8071	16.17
	0.7332	8.10		0.7106	18.31
	0.6412	8.52		0.6139	21.09
	0.5470	8.98		0.5171	24.78
	0.4498	9.50		0.4199	30.17
	0.3485	10.09		0.3223	37.98
	0.2417	10.75		0.2235	50.93
	0.1267	11.52		0.1214	75.65
	0	12.35		0.0664	101.21
				0	141.11

TABLE IV. (Continued)

System	v_2	$\alpha^{\rm el}_{\rm calcd}$ joule/cc.
n-Butylchloride —Cyclohexane	1.000	9.34
	0.9080	10.08
	0.8154	11.18
	0.7227	12.17
	0.6278	13.11
	0.5323	14.25
	0.4350	15.63
	0.3352	17.33
	0.2315	19.44
	0.1214	22.12
	0	25.22
n-Butylcyanide —Cyclohexane	1.000	17.50
	0.9038	18.57
	0.8074	20.50
	0.7109	22.83
	0.6143	25.79
	0.5173	29.54
	0.4199	34.65
	0.3216	41.83
	0.2218	52.64
	0.1181	70.32
	0.0625	87.26
	0	109.10
Diethyl ketone (Methyl propyl ketone) —Cyclohexane	1.000	8.83
	0.9045	9.48
	0.8088	10.42
	0.7129	11.55
	0.6167	12.95
	0.5202	14.36
	0.4230	17.10
	0.3248	20.77
	0.2245	25.54
	0.1196	32.54
	0.0632	38.65
	0	46.69
Cyclohexanone —Cyclohexane	1.000	9.81
	0.8991	10.41
	0.8039	11.45
	0.7084	12.70
	0.6127	14.27
	0.5165	16.28
	0.4197	18.16
	0.3217	22.62
	0.2216	28.01
	0.1157	36.60
	0.0583	43.69
	0	52.08

System	v_2	$\alpha^{\rm el}_{\rm calcd}$ joule/cc.
Chlorocyclohexane —Methylcyclohexane	1.000	7.10
	0.9091	7.04
	0.8176	7.53
	0.7253	8.10
	0.6320	8.77
	0.5373	9.55
	0.4407	10.48
	0.3411	11.61
	0.2371	13.04
	0.1256	14.90
	0	17.15
Bromocyclohexane —Methylcyclohexane	1.000	7.14
	0.9098	7.37
	0.8190	7.87
	0.7273	8.44
	0.6345	9.12
	0.5403	9.91
	0.4439	10.84
	0.3444	11.98
	0.2401	13.41
	0.1277	15.23
	0	17.37
cis-Dichloroethylene —*trans*-Dichloroethylene	1.000	15.23
	0.9062	15.97
	0.8120	17.12
	0.7236	18.34
	0.6213	20.00
	0.5244	21.91
	0.4257	24.19
	0.3244	27.04
	0.2188	30.71
	0.1056	35.62
	0	40.74
Pyridine —1,4-Dioxane	1.000	15.44
	0.9083	15.73
	0.8163	17.04
	0.7237	18.57
	0.6306	20.41
	0.5365	22.69
	0.4411	25.52
	0.3436	29.18
	0.2425	34.09
	0.1346	41.19
	0	51.24

TABLE V. THE ELECTROSTATIC PART OF VAN LAAR COEFFICIENTS, $\alpha^{\text{el}}_{\text{calcd}}$ CALCULATED ACCORDING TO ONSAGER'S MODEL FOR BINARY SYSTEMS CONSISTING OF POLAR AND AROMATIC NON-POLAR MOLECULES

System	v_2	$\alpha^{\text{el}}_{\text{calcd}}$ joule/cc.	System	v_2	$\alpha^{\text{el}}_{\text{calcd}}$ joule/cc.
Chlorobenzene —Toluene	1.000	6.06	*n*-Butylchloride —Toluene	1.000	8.31
	0.9005	6.04		0.9004	9.10
	0.7978	6.34		0.8002	9.94
	0.6972	6.67		0.6992	10.77
	0.6011	6.98		0.5970	11.70
	0.4855	7.37		0.4934	12.78
	0.3747	7.81		0.3878	14.06
	0.2595	8.33		0.2792	15.62
	0.1371	8.92		0.1661	17.58
	0.0051	9.59		0.0456	20.21
	0	9.67		0	21.03
Bromobenzene —Toluene	1.000	6.61	*n*-Butylcyanide —Toluene	1.000	16.65
	0.9007	6.79		0.9014	17.91
	0.7998	7.29		0.8028	19.78
	0.6972	7.45		0.7039	22.09
	0.5923	7.83		0.6049	24.99
	0.4844	8.25		0.5055	28.77
	0.3727	8.71		0.4057	33.87
	0.2557	9.17		0.3050	41.16
	0.1315	9.51		0.2026	52.51
	0	9.64		0.0961	72.80
				0.0388	79.91
				0	91.86
Benzonitrile —Toluene	1.000	21.37	Cyclohexanone —Toluene	1.000	8.93
	0.9027	22.46		0.8963	8.61
	0.8053	24.58		0.7985	10.53
	0.7077	27.20		0.7004	11.71
	0.6099	30.45		0.6021	13.18
	0.5114	34.65		0.5032	15.36
	0.4131	40.18		0.4036	17.54
	0.3136	47.92		0.3028	20.99
	0.2082	60.20		0.1994	26.10
	0.1056	79.09		0.0901	34.09
	0.0470	95.65		0.0303	40.48
	0	112.10		0	44.22
Nitrobenzene —Toluene	1.000	12.41	Pyridine —Benzene	1.000	15.74
	0.9023	13.26		0.9068	15.44
	0.8045	14.87		0.8133	16.72
	0.7066	16.86		0.7194	18.32
	0.6086	19.42		0.6249	20.19
	0.5104	22.87		0.5294	22.47
	0.4119	27.75		0.4328	25.35
	0.3128	35.02		0.3341	29.07
	0.2124	47.09		0.2321	34.08
	0.1085	69.87		0.1235	41.32
	0.0521	93.30		0	50.97
	0	122.20			

By differentiation with temperature, we obtain

$$\frac{d\varepsilon_1}{dT}=\frac{1}{\rho}\frac{d\rho}{dT}\frac{(\varepsilon_1-1)(\varepsilon_1+2)}{3} \qquad (24)$$

which can be calculated from the values of ε_1 and the thermal expansion coefficient of the non-polar liquid.

The values used for the calculations are shown in Table I.

The Results and Discussions

The calculation is carried out for the systems for which the heats of mixing were measured. For the systems where toluene is the non-polar component, it is assumed that the dipole-moment of toluene is zero. No serious difference occurs even if the finite value of its dipole moment is taken into account (the difference being only 4% at most). The results obtained are shown in Tables II and III and some of them are shown in Figs. 1—3.

As is seen from the above tables, the electrostatic part of the excess free energy and the excess enthalpy of mixing for the above systems derived on the Onsager model, are all positive over all the concentrations and the quantities for 1 mol. of mixture deviate from the parabola expressed by $Kx_2(1-x_2)$, where K is a constant and x_2 is the mole fraction of the polar components. The larger the dipole moments of the polar components are, the larger are the deviations and the larger the shift of $x_{\max}$, $x_{\max}$ designating the concentration where these quantities are maximum.

The electrostatic part of the excess entropy of mixing for 1 mol. of the mixture shows a specific behavior. For the systems containing polar components of small dipole moments, they are positive over the whole concentration, but for those of large dipole moments, the values are negative over the range of larger values of x_2, and rapidly increase and take very large positive values as x_2 decreases.

It is naturally expected that these values do not differ so much if the non-polar component, cyclohexane, is replaced by toluene, because of the similar dielectric constant, since according to the assumption of the theory the values are the function of dielectric constant only.

The calculated values of the electrostatic part of van Laar coefficients $\alpha^{\mathrm{el}}_{\mathrm{calcd}}$ were also calculated by the relation: $\alpha^{\mathrm{el}}_{\mathrm{calcd}}=H^{\mathrm{Eel}}_{\mathrm{calcd}}/v_2(1-v_2)\cdot V$, where V is the molar volume of the mixture. They are shown in Tables IV and V.

It is seen from the results that the values of $\alpha^{\mathrm{el}}_{\mathrm{calcd}}$ are positive and increase with the decrease of concentration x_2 of polar component, and the larger the dipole moments, the larger the values of $\alpha^{\mathrm{el}}_{\mathrm{calcd}}$ as well as their variations with concentration.

Summary

The electrostatic part of the excess functions for 21 binary systems consisting of polar and non-polar liquids were calculated according to Onsager's model. The electrostatic part of the excess free energy and excess enthalpy are positive over all the concentrations for all of these systems and these quantities are unsymmetric with regard to the mole fractions x against the value at the point $x=0.5$.

The concentrations $x_{\max}$ where these quantities have maximum values, shift to a lower concentration of polar component. The larger the dipole moment of the polar components, the larger the maximum values and the shifts are. The electrostatic part of excess entropies have positive values over the whole concentration for systems consisting of a polar component of small dipole moment, but for those consisting of one with a larger dipole moment, these quantities take negative values for a high concentration of polar component, but take positive values for a low concentration range. The electrostatic part of van Laar coefficients is also calculated and these values increase with the decrease of concentration of polar component.

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