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Heats of Mixing for Binary Mixtures. V

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The heats of mixing were measured at 25.0°C for binary mixtures of chloroform+tetrahydrofuran, + furan, and +2-methyl furan systems and for cyclohexane+chloroform, +tetrahydrofuran, +furan, and +2-methyl furan systems. Using these data and the treatment described in a previous paper [*Bull. Chem. Soc. Japan*, **37**, 1776 (1964)], the intermolecular hydrogen bond energies between chloroform and cyclic ethers were estimated to be $\Delta H=-12$ kJ for the chloroform-tetrahydrofuran-cyclohexane system, $\Delta H=-4$ kJ for the chloroform -2-methyl furan-cyclohexane system, and $\Delta H=-3$ kJ for the chloroform-furan-cyclohexane system. From these results, two types of intermolecular hydrogen bonds between chloroform and cyclic ethers are discussed.

In recent years, extensive studies have been made of the relative strengths of hydrogen bonds formed between alcohols, haloform, and oxygen- and nitrogen-containing Lewis bases. Using a number of techniques, such as infrared spectra,(1) NMR spectra,(2) refractive indices(3) and heats of solution,(4) the equilibrium constants and enthalpies for these complexes have been determined.

We estimated the enthalpy of OH-π type hydrogen bonds from our measurements of the heats of mixing for aromatic alcohol (including *m*-cresol)-aromatic hydrocarbon and aromatic alcohol-cyclohexane.(5) This paper is a continuation of our previous work.(5) The enthalpies of intermolecular hydrogen bonds between chloroform and cyclic ether will be estimated by a method similar to that described in another previous paper.(6)

Experimental

The calorimeter used in this study was a model CM-502 microcalorimeter (Applied Electric Lab. Ltd., Tokyo).(5,7) For the present work, two metal solution cells supported from the lids of an aluminum block by a framework were removed and replaced by copper mixing-cell holders with glass-mixing cells. The shape of the mixing cell was similar to that used by Larkin and McGlashan;(8) it is shown schematically in Fig. 1. Initially, the two components to be mixed were separated by a longitudinal partition and by mercury. The mixing was performed by rotating the calorimeter assembly back and forth through a 180° arc, as has been described in a previous paper.(5)

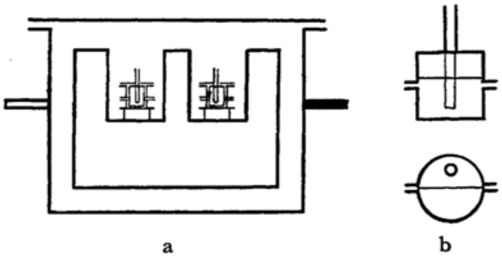

Fig. 1. a. Calorimeter. b. Cross section and upper side view of mixing cell.

The chloroform was washed with concentrated sulfuric acid and a dilute sodium hydroxide solution. Then it was dried over potassium carbonate and distilled before use. Tetrahydrofuran, furan, and 2-methyl furan were supplied by the Kaō Soap Co., Ltd.; all these materials were fractionally distilled before use. The cyclohexane was purified by the method described previously.(5) The purity of all the materials was examined by gas chromatography. The results showed only a single peak.

The physical constants of these materials are given in Table 8.

Results and Discussion

The results of the experimental measurement of the heats of mixing for the seven systems at 25.0°C are given in Tables 1—7, where x_1 is the mole fraction of the component 1; w_i ($i=1$ or 2) is the mass of the component i; Q is the quantity of heat produced during the mixing process, and $\Delta H^M_{x_1}$ and ΔH^M are the heats of mixing per mole of the

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1) Z. Yoshida and E. Ōsawa, *J. Am. Chem. Soc.*, **88**, 4019 (1966); M. R. Basila, E. L. Sair and L. R. Cousins, *ibid.*, **87**, 1665 (1965).

2) F. J. Cioffi and S. T. Zenchelsky, *J. Phys. Chem.*, **67**, 357 (1963).

3) Z. Yoshida and E. Ōsawa, This Bulletin, **38**, 140 (1965).

4) M. Tamres, *J. Am. Chem. Soc.*, **74**, 3375 (1952).

5) S. Murakami and R. Fujishiro, This Bulletin, **40**, 1784 (1967).

6) S. Murakami, K. Amaya and R. Fujishiro, This Bulletin, **37**, 1776 (1964).

7) K. Amaya and S. Hagihara, the first Japanese Calorimetry Meeting, Osaka, 1965.

8) J. A. Larkin and M. L. McGlashan, *J. Chem. Soc.*, **1961**, 3425.

component 1 and per mole of the mixture respectively.

A comparison of our data with those recorded in the literature is only possible for the chloroform-tetrahydrofuran and chloroform-cyclohexane systems. In the former case, our value for ΔH^{M} at an equimolar mixture agrees with that of Tamres, 677 cal at 25°C.[9] On the other hand, in the latter case, our data agree with those of Baud[10] over the whole concentration range except for around $x_1=0.7$, although his data were measured between 15 to 20°C.

The experimental data for $\Delta H^{\mathrm{M}}_{x_1}$ have been plotted against the mole fraction, x_1, in Figs. 2 and 3. By smoothing and extrapolating the curve to an infinite dilution $(x_1 \to 0)$ for each system,

TABLE 1. HEAT OF MIXING OF CHLOROFORM (1) AND TETRAHYDROFURAN (2) AT 25.0°C

w_1 (g)	w_2 (g)	x_1	Q (J)	$-\Delta H^{\mathrm{M}}_{x_1}$ (kJ/mol)	$-\Delta H^{\mathrm{M}}$ (J/mol)
3.1976	0.0923	0.9544	12.84	0.4795	457.7
1.5688	0.0955	0.9085	12.89	0.9811	893.7
1.5885	0.0938	0.9109	12.70	0.9623	869.9
1.5414	0.1520	0.8597	19.69	1.525	1310
0.7067	0.1477	0.7430	18.02	3.047	2262
1.4944	0.4005	0.6927	43.76	3.495	2429
0.9703	0.4045	0.5917	37.26	4.582	2713
0.6587	0.3945	0.5021	30.87	5.594	2809
0.6464	0.6314	0.3821	36.46	6.732	2573
0.5987	1.4388	0.2009	40.46	8.079	1624
0.1874	0.9848	0.1032	12.61	8.030	828.9
0.2265	0.9595	0.0653	16.05	8.456	554.8

TABLE 2. HEAT OF MIXING OF CHLOROFORM (1) AND FURAN (2) AT 25.0°C

w_1 (g)	w_2 (g)	x_1	Q (J)	$-\Delta H^{\mathrm{M}}_{x_1}$ (kJ/mol)	$-\Delta H^{\mathrm{M}}$ (J/mol)
1.7009	0.0471	0.9535	0.702	0.049	46.9
3.0837	0.1293	0.9315	1.989	0.077	71.5
1.5962	0.1191	0.8843	1.518	0.113	100.4
1.6199	0.1410	0.8695	1.944	0.143	124.3
1.3313	0.2544	0.7490	2.721	0.244	182.8
0.8686	0.2840	0.6356	2.409	0.331	210.4
0.9787	0.4407	0.5557	3.098	0.382	212.5
0.4545	0.8744	0.5232	2.892	0.395	206.7
0.6600	0.6057	0.3864	2.627	0.469	181.1
0.4107	0.7876	0.2290	1.819	0.528	121.3
0.2047	1.1137	0.0949	0.938	0.547	51.9
0.1273	1.1235	0.0607	0.551	0.515	31.4

TABLE 3. HEAT OF MIXING OF CHLOROFORM (1) AND 2-METHYL FURAN (2) AT 25.0°C

w_1 (g)	w_2 (g)	x_1	Q (J)	$-\Delta H^{\mathrm{M}}_{x_1}$ (kJ/mol)	$-\Delta H^{\mathrm{M}}$ (J/mol)
0.1665	0.8220	0.1223	1.993	1.428	174.7
0.2378	0.6763	0.1947	2.565	1.288	250.8
0.5642	0.8126	0.3232	5.513	1.166	377.0
0.6162	0.6075	0.4109	5.255	1.018	418.4
0.8779	0.4488	0.5736	5.634	0.766	439.5
1.2416	0.3675	0.6991	5.927	0.570	398.5
1.2731	0.1153	0.8837	2.309	0.217	192.1

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[9] M. Tamres, *J. Am. Chem. Soc.*, **73**, 3704 (1951).

[10] E. Baud, *Bull. Soc. Chim. France*, **17**, 329 (1915).

TABLE 4. HEAT OF MIXING OF CHLOROFORM (1) AND CYCLOHEXANE (2) AT 25.0°C

w_1 (g)	w_2 (g)	x_1	Q (J)	$-\Delta H^M_{x_1}$ (kJ/mol)	ΔH^M (J/mol)
1.1833	0.0986	0.8939	2.732	0.273	146.4
1.0467	0.2240	0.7671	5.109	0.582	446.9
0.8337	0.2846	0.6722	5.874	0.841	565.7
0.7483	0.4237	0.5545	6.912	1.103	611.7
0.5457	0.5253	0.4227	6.816	1.491	630.5
0.6962	0.9819	0.3332	9.937	1.705	567.8
0.4729	0.6861	0.3270	7.079	1.787	584.5
0.3277	0.6584	0.2597	5.389	1.963	510.0
0.2048	1.1957	0.1077	4.163	2.427	261.5
0.1839	1.6153	0.0738	3.724	2.417	179.5
0.1011	1.9255	0.0357	2.081	2.453	87.4

TABLE 5. HEAT OF MIXING OF TETRAHYDROFURAN (1) AND CYCLOHEXANE (2) AT 25.0°C

w_1 (g)	w_2 (g)	x_1	Q (J)	$\Delta H^M_{x_1}$ (kJ/mol)	ΔH^M (J/mol)
0.8603	0.0967	0.9068	2.974	0.266	241.2
0.8209	0.2055	0.8234	5.747	0.505	415.7
0.4930	0.3198	0.6427	7.274	1.064	683.8
0.4316	0.3458	0.5929	7.136	1.192	706.9
0.3576	0.4867	0.4546	7.899	1.639	745.0
0.2635	0.6788	0.3118	7.492	2.051	639.3
0.2039	0.6171	0.2781	6.280	2.224	618.3
0.2559	1.7158	0.1433	8.944	2.623	375.9
0.0829	1.9460	0.0474	3.385	2.946	139.7

TABLE 6. HEAT OF MIXING OF FURAN (1) AND CYCLOHEXANE (2) AT 25.0°C

w_1 (g)	w_2 (g)	x_1	Q (J)	$\Delta H^M_{x_1}$ (kJ/mol)	ΔH^M (J/mol)
0.9315	0.2019	0.8546	9.774	0.693	592.3
0.4863	0.3153	0.6627	11.431	1.552	1029.9
0.4122	0.4619	0.5319	13.336	2.137	1136.8
0.3866	0.4863	0.5031	13.516	2.310	1162.0
0.2113	0.5274	0.3379	9.405	2.941	993.3
0.1428	0.7019	0.2058	7.861	3.638	748.4
0.1047	1.1349	0.1051	6.343	4.005	504.7
0.0864	1.5444	0.0665	5.428	4.153	296.2
0.0748	1.5288	0.0587	4.782	4.224	247.9

shown in Figs. 2 and 3, we can obtain the heats of mixing at an infinite dilution ($\lim_{x_1\to 0} \Delta H^M_{x_1}$). They are as follows: 2.70 kJ for the chloroform(1)+cyclohexane(2) system; 3.15 kJ for the tetrahydrofuran(1)+cyclohexane(2) system; 4.20 kJ for the 2-methyl furan(1)+cyclohexane(2) system; 4.50 kJ for the furan(1)+cyclohexane(2) system, −9.20 kJ for the chloroform(1)+tetrahydrofuran(2) system; −1.56 kJ for the chloroform(1)+2-methyl furan(2) system; and −0.57 kJ for the chloroform(1)+furan(2) system.

The values of $\lim_{x_1\to 0} \Delta H^M_{x_1}$ in the cyclohexane series provide energies sufficient to break up all the interactions existing between molecules in the pure state, that is, dipole-dipole interaction in chloroform and tetrahydrofuran, and dipole-dipole and π-π interactions in 2-methyl furan and furan.

In a previous paper,⁶⁾ we estimated the energies of dipole-dipole interaction in *n*-ether, ketones, and tertiary amine as the difference in the dipolar stabilization energy of the dipole arising from the reaction field with different media in Onsager's

TABLE 7. HEAT OF MIXING OF 2-METHYL FURAN (1) AND CYCLOHEXANE (2) AT 25.0°C

w_1 (g)	w_2 (g)	x_1	Q (J)	$\Delta H^M_{x_1}$ (kJ/mol)	ΔH^M (J/mol)
0.7752	0.1380	0.8521	5.339	0.566	481.8
0.6164	0.2031	0.7567	6.958	0.927	701.3
0.5816	0.2761	0.6815	8.205	1.158	791.6
0.5945	0.3281	0.6507	9.530	1.315	856.5
0.4207	0.4143	0.5101	9.435	1.841	939.0
0.3854	0.5303	0.4269	10.429	2.222	948.6
0.2694	0.5901	0.3188	8.534	2.601	829.1
0.2126	0.7271	0.2306	7.962	3.075	709.1
0.1446	0.7446	0.1660	5.776	3.280	544.5
0.0800	0.8111	0.0918	3.481	3.572	328.0
0.1000	1.0529	0.0885	4.574	3.768	333.3
0.0777	1.0220	0.0717	3.578	3.781	271.2

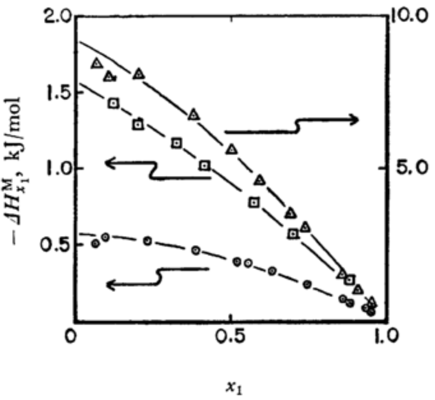

Fig. 2. Heats of mixing of $CHCl_3$+cyclic ether systems: ⊙, furan; ⊡, 2-methylfuran; ◬, tetrahydrofuran.

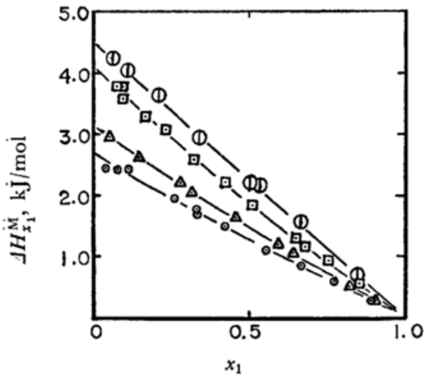

Fig. 3. Heats of mixing of polar liquid+cyclohexane systems: ⊙, $CHCl_3$; ◬, tetrahydrofuran; ⊡, 2-methylfuran; ⦶, furan.

treatment of polar liquids. The calculated results seem to agree with the $\lim_{x_1\to 0}\Delta H^M_{x_1}$ values for the polar liquid-nonpolar solvent systems. However, in the 2-methyl furan- and furan-cyclohexane systems of the present investigation, the $\lim_{x_1\to 0}\Delta H^M_{x_1}$ values differ from the results calculated by the above-described method (0.28 kJ for the furan+cyclohexane system and 0.14 kJ for the 2-methyl furan+cyclohexane system). Therefore, the furan derivatives seem to have another interaction, such as a π-π interaction due to a π-electron of the furan nucleus. The energies of such π-π interaction in furan derivatives can not be estimated directly. However, it seems reasonable to regard the value evaluated by subtracting the dipole-dipole interaction energy from the $\lim_{x_1\to 0}\Delta H^M_{x_1}$ value as the energy of π-π interaction—that is, 4.22 kJ (4.50−0.28) for the furan+cyclohexane system and 4.06 kJ (4.20−0.14) for the 2-methyl furan+cyclohexane system.

On the other hand, the values of $\lim_{x_1\to 0}\Delta H^M_{x_1}$ in the chloroform series represent the energies of transfer from the pure chloroform state to one in which each chloroform molecule make a hydrogen bond with an ether molecule, and in which such associated complex molecules are surrounded by a large amount of the ether medium.

Although there are various methods for estimating the energy of the intermolecular interaction, we can estimate the energies of intermolecular hydrogen bonds between chloroform and cyclic ethers in the same way as has been described in a previous paper.[6)]

Of the enthalpy cycle shown in Fig. 7 of Ref. 6, ΔH_1, ΔH_2, and ΔH_3 are also measured in the present work, while ΔH_4 in Process 4 is estimated by the same treatment as has been described previously.[6)] In the tetrahydrofuran case, two energy changes will contribute to ΔH_4. One, the heat of the mixing of $(x-1)$ mol of tetrahydrofuran with a large quantity of cyclohexane, is equal to $(x-1)\ \Delta H_2$, and the other is ΔH_4^d, due to the enthalpy change from the state in which the associated complex molecules are surrounded by the ether medium to

TABLE 8. PHYSICAL CONSTANTS OF SUBSTANCES NECESSARY FOR THE CALCULATION OF DIPOLAR ENERGIES

	t°C	n_D	d	ε	μ	μ_{12}
Chloroform	20	1.4456	1.4892	4.791	1.22D	
	25	1.4429	(1.4809)	4.724		
	30	1.4339	1.4706	4.653		
Tetrahydrofuran	20	1.4071	0.8892	7.521	1.77D[c]	2.53D[c]
	25	1.4041	0.8823	7.402		
	30	1.4020	0.8773	7.252		
Furan	20	1.4215	0.937[a]	2.954[b]	0.67D[d]	(1.39D)
	25	1.4181	0.913	2.932		
	30	1.4152	(0.899)	2.910		
2-Methylfuran	20	1.4320	0.91365	2.742	0.70D[d]	(1.41D)
	25	1.4295	0.90779	2.716		
	30	1.4265	0.90202	2.693		

a) J. A. Riddick and E. E. Toops, Jr., "Organic solvents," second edition, Interscience Publishers, N. Y. (1955).

b) P. Smyth *et al.*, *J. Phys. Chem.*, **59**, 1088 (1955).

c) A. Weisbecker, *J. Chim. Phys.*, **62**, 1170 (1966).

d) A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco (1964).

that in which they are surrounded by the cyclohexane medium. On the other hand, in furan derivatives, another contribution to ΔH_4 comes from the π-π interaction of the associated complex molecules. As this contribution can not be estimated, we shall assume it to be equal to the energies of the π-π interaction in the furan derivative. The contribution due to $\Delta H_4{}^d$ may be calculated by the previously-described method. The physical constants necessary for this calculation are summarized in Table 8, where d, ε, n_D, and μ are the density, dielectric constant, refractive indices, and dipole moment respectively. μ_{12} is the dipole moment of the associated complex molecule. Its value for the tetrahydrofuran system was derived by Weisbecker.[11] He determined it by assuming that a hydrogen atom of chloroform forms a hydrogen bond with an oxygen atom of tetrahydrofuran. On the other hand, the μ_{12} values for the furan derivative systems were calculated by assuming that a chloroform molecule combines on the nucleus of furan and by the vector addition of the dipoles of two component molecules. The reasons for this assumption will be given later.

The $\Delta H_4{}^d$ values thus obtained are as follows: 3.08 kJ for the chloroform-tetrahydrofuran complex; 0.38 kJ for the chloroform-furan complex; 0.35 kJ for the chloroform-2-methyl furan complex; 0.28 kJ for the furan-cyclohexane system, and 0.14 kJ for the 2-methyl furan-cyclohexane system.

By using the $\Delta H_4{}^d$ values calculated above and the other measured values, the intermolecular hydrogen bond energies between chloroform and cyclic ethers, ΔH_5, are found to be:

for the chloroform-tetrahydrofuran-cyclohexane system:

$$\begin{aligned}\Delta H_5 &= -\Delta H_1 - x\Delta H_2 + \Delta H_3 + \Delta H_4\\ &= -\Delta H_1 - x\Delta H_2 + \Delta H_3 + (x-1)\Delta H_2\\ &\quad + \Delta H_4{}^d\\ &= -2.70 - 3.15x - 9.20 + 3.15(x-1)\\ &\quad + 3.08\\ &= -11.97\ \mathrm{kJ};\end{aligned}$$

for the chloroform-furan-cyclohexane system:

$$\begin{aligned}\Delta H_5 &= -\Delta H_1 - x\Delta H_2 + \Delta H_3 + \Delta H_4\\ &= -\Delta H_1 - x\Delta H_2 + \Delta H_3 + (x-1)\Delta H_2\\ &\quad + \Delta H_{\pi-\pi} + \Delta H_4{}^d\\ &= -2.70 - 4.50x - 0.57 + 4.50(x-1)\\ &\quad + 4.22 + 0.38\\ &= -3.17\ \mathrm{kJ},\ \text{and}\end{aligned}$$

for the chloroform-2-methyl furan-cyclohexane system:

$$\begin{aligned}\Delta H_5 &= -2.70 - 4.20x - 1.56 + 4.20\,(x-1)\\ &\quad + 4.06 + 0.35\\ &= -3.99\ \mathrm{kJ}.\end{aligned}$$

As may be seen in the above calculations, the energies of the intermolecular hydrogen bonds between chloroform and cyclic ethers are in the order: tetrahydrofuran > 2-methyl furan > furan.

Let us now consider this order. In furan derivatives, π-electron is present, but not in tetrahydrofuran. Therefore, furan has a negative net charge on the ring carbon and a positive net charge on the oxygen atom, as is shown in Fig. 4.[12] The hydrogen-bond forming power of furan with chloroform will be weakened. On the other hand, it is known that the tetrahydrofuran molecule makes

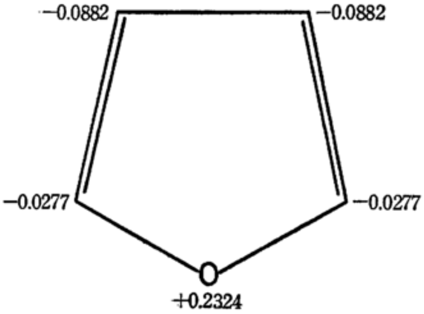

Fig. 4. Net charge on the atoms of furan molecule.

a CH–O type intermolecular hydrogen bond with chloroform.11) Generally, the hydrogen bond strength is stronger in the H–O type than in the H–π type.13) As the introduction of a methyl group to the furan ring causes an increase in basicity, the hydrogen bond energy for the 2-methyl furan system increases in comparison with that for the furan system. Furthermore, it is known from the spectroscopic study that the shift in the frequency of the O–H band, $\Delta\nu$, of alcohol is correlated with the hydrogen-bond energy. The frequency shifts, $\Delta\nu$, of phenol due to hydrogen bonding with some heteroaromatics were measured in carbon tetrachloride.1) The results were arranged in the order of: tetrahydrofuran$>$2-methyl furan$>$furan; this order is consistent with that one which we have estimated on the basis of the thermochemical measurements.

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11) A. Weisbecker, *J. Chim. Phys.*, **62**, 1170 (1966).
12) K. Nishimoto, private communication.
13) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco (1960); R. West, International Symposium on Molecular Structure and Spectroscopy, Tokyo, 1962.