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# Thermochemical Evidence of OH-$\pi$ Type Intermolecular Hydrogen Bonds

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A calorimeter for measuring the heat of mixing was constructed. Using the calorimeter, the heats of mixing were measured at 25.0±0.01°C for binary mixtures of benzyl alcohol with ethyl benzene or cyclohexane and ethyl benzene with cyclohexane, and at 35.0±0.01°C for binary mixtures of *m*-cresol with *m*-xylene or cyclohexane and *m*-xylene with cyclohexane. By plotting the values of the heats of mixing, $\Delta H_{x_1}{}^{\mathrm{M}}$, against the mole fraction of component 1, $x_1$, and by extrapolating the curve to an infinite dilution ($x_1 \rightarrow 0$) for each system, the heats of mixing at an infinite dilution ($\lim_{x_1\rightarrow 0} \Delta H_{x_1}{}^{\mathrm{M}}$) were obtained graphically. By using the values of $\lim_{x_1\rightarrow 0} \Delta H_{x_1}{}^{\mathrm{M}}$ obtained for these systems and by applying an enthalpy cycle, the OH-$\pi$ type intermolecular hydrogen bond energies were estimated to be $\Delta H = -6.2$ kJ for the benzyl alcohol-ethyl benzene - cyclohexane system and $\Delta H = -13.1$ kJ for the *m*-cresol - *m*-xylene - cyclohexane system. The results obtained have been discussed from two points of view, that is, the proton-donating power of alcohols and the proton-accepting power of aromatic hydrocarbons.

It is well known, from the analysis of the thermodynamic and spectroscopic data, that aromatics form hydrogen bonds with acids.[1,2] In recent years, a number of techniques, such as infrared spectra,[3] NMR spectra,[4] refractive indices[5] and heat of solution,[6] have been developed for the study of this type of hydrogen bond. Using the above methods, the equilibrium constants and enthalpies of OH-$\pi$ type hydrogen bonds for various acid-base systems have been determined. However, there have been only a few works attempting to determine the enthalpies from the direct calorimetry. This paper will present a calorimetric method to determine the enthalpy of OH-$\pi$ type hydrogen bonds from the measurement of the heat of mixing for aromatic alcohol (including *m*-cresol)-aromatic hydrocarbon and aromatic alcohol-cyclohexane.

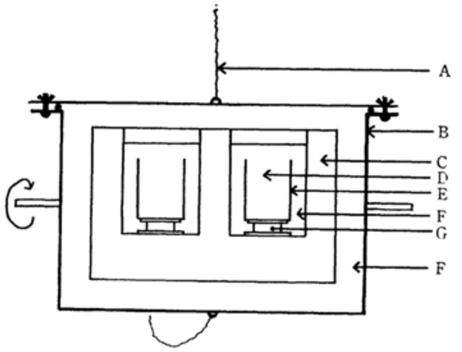

Fig. 1. Calorimeter.

| | | | |
|---|---|---|---|
| A | String | B | Submarine chamber |
| C | Iron block | D | Mixing cell |
| E | Mixing cell holder | | |
| F | Thermal insulator | | |
| G | Thermomodule | | |

The samples used are benzyl alcohol, *m*-cresol, ethyl benzene, *m*-xylene, and cyclohexane.

## Experimental

The calorimeter for measuring heats of mixing is shown in Fig. 1 schematically. It is similar to the Tian-Calvet type,[7] but the thermopile is replaced with a thermomodule, HTM 0156 type (Sharp Electric Co., Ltd., Osaka), in order to detect a smaller temperature change.

The mixing cell is a modification of the previous one, with a pocket into which the heating coil is inserted.[8] Initially the two components to be mixed are separated by mercury. The mixing is performed by rotating the cell back and forth in a small space several times through the manipulation of the strings at the lid and at the bottom of the submarine chamber.

For the calibration of the calorimeter, a measured quantity of electric energy was introduced into the

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[1] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Company, San Francisco (1960).

[2] J. S. Rowlinson, "Liquids and Liquid Mixtures," Butherworth and Co., Ltd., London (1959).

[3] Z. Yoshida and E. Ōsawa, *J. Am. Chem. Soc.*, **87**, 1467 (1965); M. R. Busila, E. L. Sair and L. R. Cousins, *ibid.*, **87**, 1665 (1965).

[4] E. Lippert, *Ber. Bunsenges. Physik. Chem.*, **67**, 267 (1963).

[5] Z. Yoshida and E. Ōsawa, This Bulletin, **38**, 140 (1965).

[6] M. Tamres, *J. Am. Chem. Soc.*, **74**, 3375 (1952).

[7] E. Calvet and H. Prat, "Recent Progress in Microcalorimetry," Pergamon Press, London (1963).

[8] S. Murakami and R. Fujishiro, This Bulletin, **39**, 720 (1966).

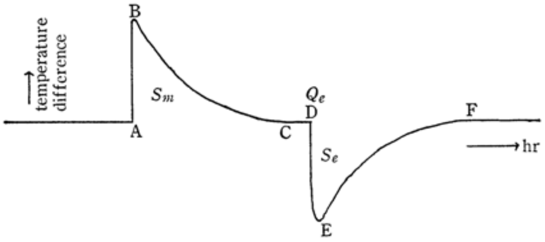

Fig. 2. A typical recording chart of heat of mixing.

heating coil after the curve for mixing had come completely back to the "experimental zero" line. A typical recording chart is shown in Fig. 2. Mixing was made at the point "A," and the cooling curve was drawn from "B" to "C." At the point "D" an amount of electric energy approximately equal to the quantity of heat absorbed on the mixing of the samples was dissipated in the heating coil.

The heat of mixing per mole of component 1, $\Delta H_{x_1}{}^{M}$, was calculated using the following relation.

$$\Delta H_{x_1}{}^{M} = Q/n_1 = (Q_e \times S_m/S_e)/n_1 \tag{1}$$

where $n_1$ is the number of the mole of the component 1; $Q_e$ is the amount of electric energy dissipated in the heating coil; $S_m$ is the area surrounded by the mixing curve and the base line, and $S_e$ is that surrounded by the corresponding heating curve and base line. These area were estimated from the average weight of three sheets of paper which were copied by a copying press (Copystar, Mita Co., Ltd., Osaka) and were cut off along the curve.

In order to check the accuracy of the calorimeter, the heat of mixing was measured with the benzene+carbon tetrachloride system at 25.0±0.01°C; the advantages of this system, as a test system have already been extensively discussed.[9,10] Most of the measurements of this system were made with a single-type calorimeter which consisted of a half of a twin-type calorimeter. Two experimental techniques were used, one was the "weighing area" procedure described above, while the other was the "thermal compensation" procedure, in which the fall in temperature is compensated for by the simultaneous introduction of a measured quantity of electric energy. The results obtained by both procedures may be represented by the following equation.

$$\Delta H_m = x(1-x)[459.6 + 16.0(1-x) + 20.2(1-2x)^2] \tag{2}$$

In Fig. 3 the results of other workers[10,11] are compared with ours. Here $\Delta H_m$ is the heat of mixing in unit of joule per mole of the mixture; $x$ is the mole fraction of carbon tetrachloride, and $\delta$ is the excess of the measured value of $\Delta H_m$ over that calculated from Eq. (2). Our results agree with those of McGlashan *et al.* and with those of Benson *et al.*

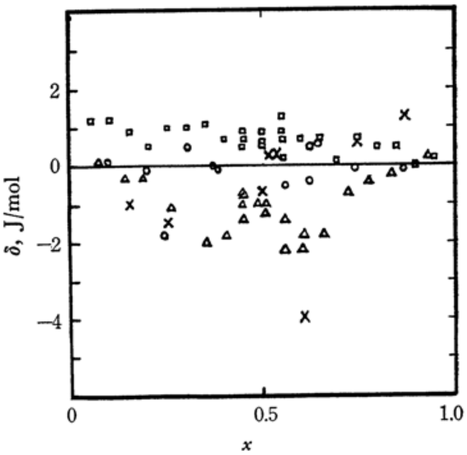

Fig. 3. The excees of heat of mixing over the value calculated according to Eq. (2) for benzene+carbon tetrachloride at 25.0°C.

○ This work (thermal compensation procedure)
× This work (weighing area procedure)
□ Larkin and McGlashan
△ Bennett and Benson

Benzyl alcohol and *m*-cresol were vigorously shaken with mercury for a long time, and then distilled under reduced pressure. Cyclohexane, ethyl benzene, and *m*-xylene were treated with concentrated sulfuric acid, and a sodium hydroxide aqueous solution, shaken with mercury, and then distilled over phosphorus pentoxide. The gas chromatographs of all the samples except for *m*-xylene showed a single peak. The result of the gas chromatography of *m*-xylene indicated the existence of a very small amount of an impurity (probably a para-isomer), but we used it without further purification.

## Results and Discussion

The results of our measurements of the six systems are given in Tables 1 to 6 and in Figs. 4 and 5, where $x_1$ is the mole fraction of the component 1; $w_1$ ($i$=1 or 2) is the mass of the component $i$; $Q$ is the measured heat of mixing, and $\Delta H_{x_1}{}^{M}$ is the heat of mixing per mole of component 1.

For the mixture of a higher mole fraction than 0.05, the heats of mixing were measured by mixing the pure liquids, while for the mixture of a lower mole fraction, they were measured by diluting a solution, whose heat of mixing was known from a previous run, with the other component "solvent."

The heats of mixing were measured at 25.0±0.01°C for binary mixtures of benzyl alcohol with ethyl benzene or cyclohexane and ethyl benzene with cyclohexane, and at 35.0±0.01°C for those of *m*-cresol with *m*-xylene or cyclohexane and *m*-xylene with cyclohexane.

By plotting $\Delta H_{x_1}{}^{M}$ against $x_1$ and by extrapolating the curve to an infinite dilution ($x_1 \rightarrow 0$) for each system, shown in Figs. 4 and 5, we can obtain the heats of mixing per mole of component 1 at

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9) H. A. Skinner, "Experimental Thermochemistry," Vol. 2, IUPAC, Interscience Publishers, London (1962).

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

11) J. E. Bennett and G. C. Benson, *Can. J. Chem.*, **43**, 1912 (1965).

an infinite dilution ($\lim_{x_1\to 0} \Delta H_{x_1}{}^{M}$). They are as follows:

25.5 kJ for the benzyl alcohol(1)+cyclohexane(2) system
16.7 kJ for the benzyl alcohol(1)+ethyl benzene(2) system
2.6 kJ for the ethyl benzene(1)+cyclohexane(2) system
27.6 kJ for the *m*-cresol(1)+cyclohexane(2) system
11.6 kJ for the *m*-cresol(1)+*m*-xylene(2) system
2.9 kJ for the *m*-xylene(1)+cyclohexane(2) system

TABLE 1. HEAT OF MIXING OF BENZYL ALCOHOL (1) AND CYCLOHEXANE (2) AT 25.0°C

| $x_1$ | $w_1$ | $w_2$ | Q(J) | $\Delta H_{x_1}{}^{M}$ kJ/mol |
|---|---|---|---|---|
| 0.9470 | 1.2471 | 0.0544 | 1.826 | 0.158 |
| 0.8140 | 1.0196 | 0.1813 | 5.882 | 0.624 |
| 0.7563 | 1.0005 | 0.2509 | 8.548 | 0.924 |
| 0.6503 | 0.8103 | 0.3392 | 9.643 | 1.287 |
| 0.4464 | 0.5007 | 0.4833 | 9.281 | 2.005 |
| 0.2561 | 0.4205 | 0.9505 | 11.73 | 3.016 |
| 0.2561 | 0.3599 | 0.8138 | 9.897 | 2.973 |
| 0.2558 | 0.4281 | 0.9693 | 11.86 | 2.995 |
| 0.1136 | 0.1459 | 0.8861 | 6.174 | 4.576 |
| 0.0587 | 0.1497 | 1.8963 | 9.882 | 7.044 |
| 0.0543 | 0.1430 | 1.9392 | 9.674 | 7.314 |
| 0.0253 | | | | 11.3 * |
| 0.0250 | | | | 11.4 * |
| 0.0146 | | | | 15.8 * |
| 0.0099 | | | | 19.6 * |
| 0.0058 | | | | 23.3 * |
| 0.0032 | | | | 23.7 * |

* $\Delta H_{x_1}{}^{M}$ were measured by the dilution method.

TABLE 2. HEAT OF MIXING OF BENZYL ALCOHOL (1) AND ETHYL BENZENE (2) AT 25.0°C

| $x_1$ | $w_1$ | $w_2$ | Q(J) | $\Delta H_{x_1}{}^{M}$ kJ/mol |
|---|---|---|---|---|
| 0.9295 | 1.3121 | 0.0977 | 2.019 | 0.166 |
| 0.7640 | 0.8357 | 0.2535 | 5.077 | 0.657 |
| 0.6451 | 0.7416 | 0.4005 | 6.923 | 1.009 |
| 0.4749 | 0.4876 | 0.5293 | 7.350 | 1.630 |
| 0.4391 | 0.5016 | 0.6285 | 8.127 | 1.752 |
| 0.2820 | 0.2464 | 0.6157 | 6.456 | 2.834 |
| 0.2572 | 0.2758 | 0.7822 | 8.174 | 3.205 |
| 0.1086 | 0.2122 | 1.7093 | 12.71 | 6.480 |
| 0.0690 | 0.1580 | 2.0922 | 12.08 | 8.269 |
| 0.0600 | 0.1440 | 2.2165 | 11.68 | 8.768 |
| 0.0400 | 0.1281 | 3.0203 | 12.16 | 10.27 |
| 0.0320 | | | | 11.0 * |
| 0.0129 | | | | 13.4 * |
| 0.0064 | | | | 15.2 * |
| 0.0036 | | | | 15.3 * |

* $\Delta H_{x_1}{}^{M}$ were measured by the dilution method.

TABLE 3. HEAT OF MIXING OF ETHYL BENZENE (1) AND CYCLOHEXANE (2) AT 25.0°C

| $x_1$ | $w_1$ | $w_2$ | Q(J) | $\Delta H_{x_1}{}^{M}$ kJ/mol |
|---|---|---|---|---|
| 0.8594 | 1.0333 | 0.1340 | 2.437 | 0.2504 |
| 0.8337 | 1.0079 | 0.1594 | 2.816 | 0.2966 |
| 0.7986 | 0.8119 | 0.2010 | 2.671 | 0.3557 |
| 0.7507 | 0.8402 | 0.2212 | 3.649 | 0.4610 |
| 0.6884 | 0.7643 | 0.2827 | 4.610 | 0.6403 |
| 0.6437 | 0.7007 | 0.3075 | 4.825 | 0.7310 |
| 0.6267 | 0.6108 | 0.2884 | 4.594 | 0.7985 |
| 0.6107 | 0.6234 | 0.3150 | 5.101 | 0.8686 |
| 0.6029 | 0.6082 | 0.3176 | 4.992 | 0.8713 |
| 0.5416 | 0.5230 | 0.3510 | 4.882 | 0.9910 |
| 0.4910 | 0.4844 | 0.3981 | 5.027 | 1.102 |
| 0.4693 | 0.5187 | 0.4650 | 5.604 | 1.147 |
| 0.4367 | 0.4045 | 0.4136 | 4.610 | 1.210 |
| 0.4092 | 0.4450 | 0.5092 | 5.255 | 1.254 |
| 0.3857 | 0.3429 | 0.4329 | 4.316 | 1.336 |
| 0.3564 | 0.3996 | 0.5720 | 5.307 | 1.408 |
| 0.2351 | 0.3459 | 0.8955 | 5.523 | 1.727 |
| 0.2234 | 0.2803 | 0.8240 | 4.753 | 1.800 |
| 0.1352 | 0.1560 | 0.7914 | 3.027 | 2.060 |
| 0.0604 | 0.0487 | 0.6004 | 1.131 | 2.46 |
| 0.0591 | 0.1388 | 1.9096 | 3.332 | 2.445 |
| 0.0384 | 0.0433 | 0.8594 | 1.042 | 2.55 |
| 0.0221 | 0.1058 | 3.8882 | 2.552 | 2.561 |

TABLE 4. HEAT OF MIXING OF *m*-CRESOL (1) AND CYCLOHEXANE (2) AT 35.0°C

| $x_1$ | $w_1$ | $w_2$ | Q(J) | $\Delta H_{x_1}{}^{M}$ kJ/mol |
|---|---|---|---|---|
| 0.8082 | 1.0100 | 0.1866 | 5.972 | 0.639 |
| 0.6724 | 0.7102 | 0.2693 | 7.549 | 1.149 |
| 0.3772 | 0.3526 | 0.4530 | 7.524 | 2.307 |
| 0.3491 | 0.4359 | 0.6324 | 10.07 | 2.499 |
| 0.1796 | 0.2537 | 0.9019 | 10.02 | 4.273 |
| 0.1054 | 0.1438 | 0.9494 | 7.265 | 5.459 |
| 0.0836 | 0.1410 | 1.2032 | 8.376 | 6.426 |
| 0.0767 | 0.1328 | 1.2443 | 8.032 | 6.544 |
| 0.0698 | 0.1292 | 1.3410 | 8.782 | 7.351 |
| 0.0632 | 0.1337 | 1.5412 | 9.734 | 7.873 |
| 0.0542 | 0.1461 | 1.9823 | 11.09 | 8.207 |
| 0.0537 | 0.1337 | 1.8340 | 10.13 | 8.193 |
| 0.0285 | 0.0973 | 2.5784 | 10.24 | 11.4 |
| 0.0277 | | | | 11.5 * |
| 0.0173 | | | | 14.8 * |
| 0.0160 | | | | 15.8 * |
| 0.0094 | | | | 19.4 * |
| 0.0048 | | | | 23.8 * |
| 0.0043 | | | | 24.2 * |
| 0.0032 | | | | 25.4 * |
| 0.0023 | | | | 26.9 * |

* $\Delta H_{x_1}{}^{M}$ were measured by the dilution method.

TABLE 5 HEAT OF MIXING OF *m*-CRESOL (1) AND *m*-XYLENE (2) AT 35.0°C

| $x_1$ | $w_1$ | $w_2$ | $Q(J)$ | $\Delta H_{x_1}{}^{M}$ kJ/mol |
|---|---|---|---|---|
| 0.8527 | 0.9910 | 0.1680 | 3.497 | 0.3816 |
| 0.6345 | 0.6930 | 0.3920 | 7.396 | 1.154 |
| 0.5777 | 0.5771 | 0.4141 | 7.478 | 1.401 |
| 0.3735 | 0.3726 | 0.6136 | 8.299 | 2.408 |
| 0.2454 | 0.2804 | 0.8464 | 9.106 | 3.512 |
| 0.1919 | 0.2021 | 0.8353 | 7.807 | 4.178 |
| 0.1020 | 0.1471 | 1.2710 | 8.059 | 5.925 |
| 0.0992 | 0.1460 | 1.2645 | 7.844 | 5.810 |
| 0.0627 | 0.1215 | 1.7821 | 7.498 | 6.674 |
| 0.0424 | 0.1046 | 2.3159 | 7.453 | 7.709 |
| 0.0270 | | | | 8.58 * |
| 0.0193 | | | | 9.25 * |
| 0.0192 | | | | 9.20 * |
| 0.0066 | | | | 10.7 * |
| 0.0051 | | | | 10.8 * |
| 0.0030 | | | | 11.1 * |

* $\Delta H_{x_1}{}^{M}$ were measured by the dilution method.

TABLE 6. HEAT OF MIXING OF *m*-XYLENE (1) AND CYCLOHEXANE (2) AT 35.0°C

| $x_1$ | $w_1$ | $w_2$ | $Q(J)$ | $\Delta H_{x_1}{}^{M}$ kJ/mol |
|---|---|---|---|---|
| 0.7180 | 0.7776 | 0.2421 | 4.171 | 0.5694 |
| 0.7092 | 0.8093 | 0.2630 | 4.302 | 0.5644 |
| 0.5738 | 0.6491 | 0.3570 | 5.115 | 0.8366 |
| 0.5289 | 0.5576 | 0.3937 | 4.886 | 0.9303 |
| 0.4488 | 0.4167 | 0.4057 | 4.717 | 1.202 |
| 0.3227 | 0.3535 | 0.5881 | 5.218 | 1.567 |
| 0.2298 | 0.2502 | 0.6648 | 4.467 | 1.895 |
| 0.0882 | 0.0952 | 0.7803 | 2.146 | 2.39 |
| 0.0342 | 0.0530 | 1.1867 | 1.368 | 2.74 |
| 0.0336 | 0.0512 | 1.2788 | 1.482 | 2.80 |

Although some theoretical methods for estimating the strong orientational effects from which an excess thermodynamic function may be deduced in terms of the intermolecular force and the properties of pure components are available,[12-15] it is difficult to find a reasonable and consistent set of interaction energies and equilibrium constants of association because these methods contain many parameters. We shall now, therefore, give another qualitative estimate of the energy of OH-$\pi$ type intermolecular hydrogen bonds.

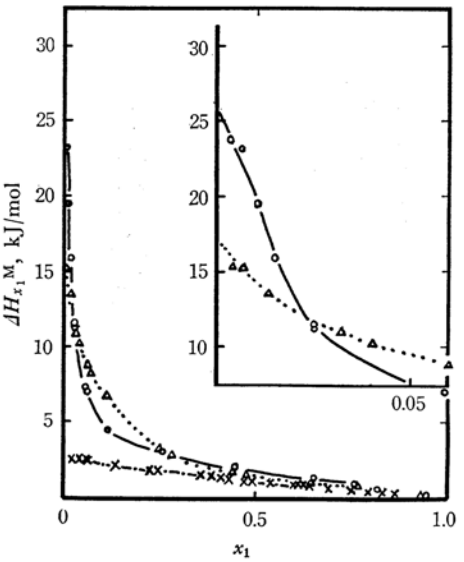

Fig. 4. Heats of mixing for benzyl alcohol-ethyl benzene-cyclohexane system.
○ Benzyl alcohol+cyclohexane
△ Benzyl alcohol+ethyl benzene
× Ethyl benzene+cyclohexane

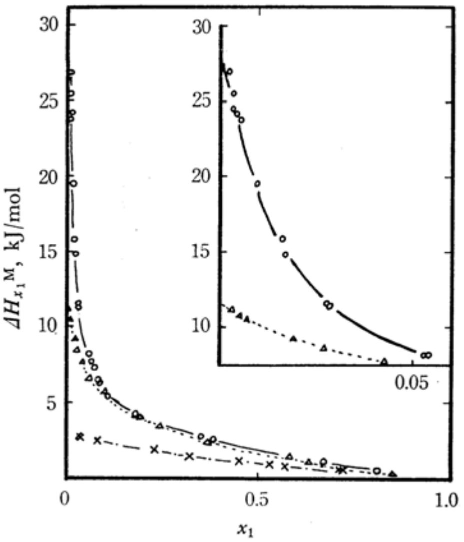

Fig. 5. Heats of mixing for *m*-cresol-*m*-xylene-cyclohexane system.
○ *m*-Cresol+cyclohexane
△ *m*-Cresol+*m*-xylene
× *m*-Xylene+cyclohexane

We considered in a previous paper[16] that, in pure alcohol, there are at least three types of stronger interactions, namely, OH-O interactions, OH-$\pi$ interactions, and $\pi$-$\pi$ interactions, due to $\pi$-electrons of the aromatic nucleus,[17] while each alcohol molecule, on infinite dilution in cyclohexane,

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[12] J. A. Barker, *J. Chem. Phys.*, **20**, 1526 (1952).

[13] L. Sarolea-Mathot, *Trans. Faraday Soc.*, **49**, 8 (1953).

[14] I. Prigogine and R. Defay, "Chemical Thermodynamics," Longmans, Green and Co., London (1954).

[15] H. Kehiaian, *Bull. Acad. Polon. Sci. ser. sci. chim.*, **11**, 487 (1963); **12**, 497 (1964).

[16] S. Murakami and R. Fujishiro, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **69**, 1627 (1966).

[17] K. Sosnkowska-Kehiaian and H. Kehiaian, *Bull. Acad. polon. Sci. ser. sci. chim.*, **13**, 659 (1965).

becomes surrounded by cyclohexane molecules and all the interactions mentioned above are broken up by the process of mixing. Therefore, the values of $\lim_{x_1\to 0}\Delta H_{x_1}{}^{\mathrm{M}}$ for the alcohol+cyclohexane systems represent the energies sufficient to break up all the interactions between molecules in pure alcohol. Similarly, since in a pure aromatic hydrocarbon such as ethyl benzene and *m*-xylene there is only a $\pi$-$\pi$ interaction, the values of $\lim_{x_1\to 0}\Delta H_{x_1}{}^{\mathrm{M}}$ for aromatic hydrocarbon+cyclohexane systems correspond to the energies of interaction between aromatic hydrocarbon and cyclohexane.

The value of $\lim_{x_1\to 0}\Delta H_{x_1}{}^{\mathrm{M}}$ for the aliphatic alcohol+hydrocarbon system is in the range of 5.0 to 6.0 kcal.[18] It is regarded as the enthalpy change when one mole of pure alcohol is completely dissociated in a solvent. The substraction of the values of $\lim_{x_1\to 0}\Delta H_{x_1}{}^{\mathrm{M}}$ for aromatic alcohol+cyclohexane systems from those for aromatic hydrocarbon+cyclohexane systems gives 5.5 kcal for benzyl alcohol and 5.9 kcal for the *m*-cresol system. These values are equal to that of aliphatic alcohol+hydrocarbon system. It seems to be more reasonable to assume that, in pure alcohol, only OH–O and $\pi$-$\pi$ interactions predominate, while OH-$\pi$ interactions will be very weak if it exists at all because, according to the spectroscopic investigations,[19] the OH-$\pi$ interaction energy is about 3 kcal or less, which is much weaker than the OH-O interaction energy (about 4—6 kcal) and the chance of forming the OH-$\pi$ interaction is very small in comparison with that of forming the OH-O interaction. Therefore, the values of $\lim_{x_1\to 0}\Delta H_{x_1}{}^{\mathrm{M}}$ for aromatic alcohol+cyclohexane system represent the enrgies sufficient to break up the OH-O and $\pi$-$\pi$ interactions. On the other hand, upon mixing alcohol with aromatic hydrocarbon, OH–O interactions in pure alcohol will be broken up by a large amount of aromatic hydrocarbon molecules and an alcohol molecule makes new OH-$\pi$ interactions with aromatic hydrocarbon molecules, as is indicated by the low value of $\lim_{x_1\to 0}\Delta H_{x_1}{}^{\mathrm{M}}$ for the *m*-cresol+*m*-xylene system.

We then carried out a treatment similar to that described in a previous paper,[20] applying the enthalpy cycle depicted in Fig. 6, and Eq. (3).

$$\Delta H_5 = -\Delta H_1 - x\Delta H_2 + \Delta H_3 + \Delta H_4 \tag{3}$$

Here, $\Delta H_1$ is the energy of breaking up the OH-O and $\pi$-$\pi$ interactions of pure alcohol by adding a large quantity of cyclohexane; $\Delta H_2$ is equal to the value of $\lim_{x_1\to 0}\Delta H_{x_1}{}^{\mathrm{M}}$ for the aromatic hydrocarbon+cyclohexane system; $\Delta H_3$, the energy change produced by the dilution of pure alcohol with a large quantity of aromatic hydrocarbon, and $\Delta H_4$ consists of two parts, one equal to $(x+1)$ $\Delta H_2$, while the other is due to the enthalpy change from the state in which OH-$\pi$ complexes are surrounded by aromatic hydrocarbon to that in which they are surrounded by cyclohexane molecules. The latter part of $\Delta H_4$ may be put at zero or neglected because the two media have almost equal dielectric constants and the dipolar stabilization energies of a complex dipole in the two media are considered to be nearly equal.

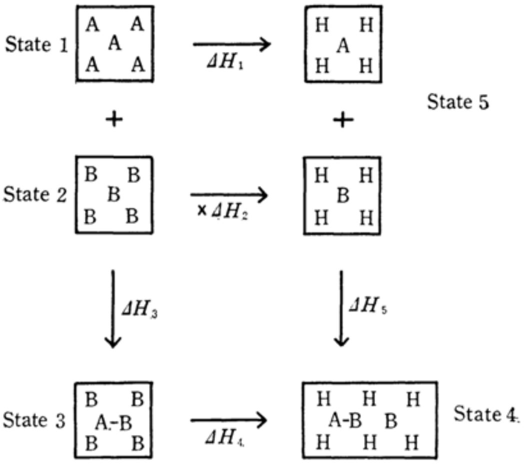

Fig. 6. Enthalpy cycle.

State 1: One mole of alcohol.
State 2: *x* mol of aromatic hydrocarbon.
State 3: One mole of A-B complex in the aromatic hydrocarbon medium, each complex being separated each other.
State 4: One mole of A-B complex and *x* mol of aromatic hydrocarbon in the cyclohexane medium.
State 5: One mole of alcohol and *x* mol of aromatic hydrocarbon in the cyclohexane medium.

The OH-$\pi$ type intermolecular hydrogen bond energies, $\Delta H_5$, for the two systems studied in this paper are found from Eq. (3) to be:

for benzyl alcohol - ethyl benzene - cyclohexane (B-E-C):

$$\begin{aligned}\Delta H_5 &= -25.5 - 2.6x + 16.7 + 2.6(x+1)\\ &= -6.2\ \mathrm{kJ}\ (-1.5\ \mathrm{kcal})\end{aligned}$$

for *m*-cresol-*m*-xylene-cyclohexane (C-X-C):

$$\begin{aligned}\Delta H_5 &= -27.6 - 2.9x + 11.6 + 2.9(x+1)\\ &= -13.1\ \mathrm{kJ}\ (-3.1\ \mathrm{kcal})\end{aligned}$$

These OH-$\pi$ type intermolecular hydrogen

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[18] J. Wolf, K. Phalke and K. Wehage, "Landolt-Böernstein, Physikalische-Chemischen Tabellen," Springer, Berlin (1936).

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bond energies, $\Delta H_5$, for the two systems are, however, obtained from the heats of mixing at different temperatures (25.0 and 35.0°C), and so they can not be directly compared with each other. However, as has been pointed out by Van Ness,[21] the $\lim_{x_1 \to 0} \Delta H_{x_1}{}^{M}$ values seem to be independent of the temperature. Therefore, the $\Delta H_5$ value obtained from these values may be regarded as being independent of the temperature.

Let us now consider the difference in the $\Delta H_5$ values between the two systems from another point of view. Two contributing factors may be considered. One is the proton-donating power of alcohol. The proton-donating power seems to be in the order of *m*-cresol > benzyl alcohol, because the dissociation constants in water for these aromatic alcohols are 10.08[22] and > 10 (benzyl alcohol is a weaker acid than phenols[23]) respectively. The other factor is the proton-accepting power.

The existence of a linear relation between the shift in the frequency of the O–H band, $\nu_{OH}$, of alcohol and the ionization potential, $I_p$, of the proton acceptor is well known from spectroscopic and theoretical studies.[24,25] If the same proton donor is used, the following relation exists.

$$I_p = a(\nu^f/\Delta\nu_{OH})^{1/2} + b \qquad (4)$$

where $\nu^f$ is the frequency of the free O–H band of alcohol and where a and b are constants. Assuming that benzyl alcohol and *m*-cresol have the same proton-donating power, the $\Delta\nu_{OH}$ for the C-X-C system is larger than that for the B-E-C systems, because the $I_p$ values of ethyl benzene and *m*-xylene are 9.12 and 9.05 eV respectively.[26] Furthermore, as the $\Delta\nu_{OH}$ is correlated with the energy of a hydrogen bond, $\Delta H_{OH-\pi}$, the intermolecular hydrogen bond energy of the C-X-C system is larger than that of the B-E-C system. Thus, the OH–$\pi$ type hydrogen bond strength with the C-X-C system may be concluded to be stronger than that with the B-E-C system. This conclusion is consistent with the results we have estimated from our thermochemical measurements.

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