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The Heats of Mixing for Binary Mixtures. III. The Intermolecular Energy of Hydrogen Bonding between Alcohol and Several Other Polar Molecules

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Calorimetric measurements of the heat of mixing have been made at 25.0±0.01°C for binary mixtures of *n*-butanol with polar liquids (acetonitrile, acetone, *n*-butyl ether, and *n*-butyl amine), and for binary mixtures of polar liquids with *n*-hexane. The calorimeter for measuring the heats of mixing was of twin type, and a thermomodule, HTM 0516 type (Sharp Electric Co., Ltd., Osaka) was used as the temperature-sensing device. By plotting the values of the heat of mixing, $\Delta H^{\mathrm{M}}_{x_1}$, 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 per mole of component 1 at an infinite dilution ($\lim_{x_1 \rightarrow 0} \Delta H^{\mathrm{M}}_{x_1}$) were obtained graphically. By using the values of $\lim_{x_1 \rightarrow 0} \Delta H^{\mathrm{M}}_{x_1}$ obtained for these systems and by using the same treatment as that described in a previous paper [S. Murakami, K. Amaya and R. Fujishiro, This Bulltein, **37**, 1776(1964)], the intermolecular hydrogen bond energies between alcohol and polar molecules were estimated; it was found that the strength of the hydrogen bond was in the following order: *n*-butyl amine>*n*-butyl ether>acetone>acetonitrile. This agrees with the results obtained from the spectroscopic study.

In previous papers,[1,2] the heats of mixing for alcohol+ketone and alcohol+hexane solutions have been measured, and from these data the hydrogen bond energy between alcohol and ketone molecules has been estimated.

In the present paper, the same treatment will be applied to the *n*-butanol+polar liquid+hexane systems, and the hydrogen bond energies between butanol and polar molecules will be estimated. Acetonitrile, acetone, *n*-butyl ether and *n*-butyl amine will be used as the polar liquids.

Experimental

The apparatus for measuring the heats of mixing is the same as that used in the previous papers,[1,2] except for replacing a 7-junction copper-constantan

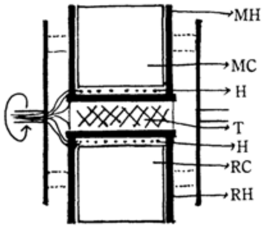

Fig. 1. Calorimeter.

MH: Mixing holder
MC: Mixing cell
H : Heater
T : Thermomodule (temperature-sensing device)
RC: Reference cell
RH: Reference holder

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

[2] M. Takami, S. Murakami and R. Fujishiro, ibid., **38**, 291 (1965).

thermocouple with a thermomodule, type HTM 0516 (Sharp Electric Co., Ltd., Osaka), in order to detect a smaller temperature change. The mixing cell and other modifications are shown schematically in Fig. 1.

The experimental procedure was similar to that described in the previous papers.[1,2]

In order to check the accuracy of our calorimeter, the heat of mixing was measured for the benzene+carbon tetrachloride system, on which the fairly accurate data of the heat of mixing had previously been obtained by Larkin and McGlashan.[3] The results obtained are shown in Fig. 2, together with those obtained by Larkin and McGlashan; here x_1 is the mole fraction of carbon tetrachloride, and ΔH^{M} is the heat of mixing expressed in joule per mole of the mixture. Our results are found to agree with those of Larkin and McGlashan within an error of only a few percent.

Alcohol, acetone, and *n*-hexane were purified in the way described previously. *n*-Butyl ether was shaken with concentrated sulfuric acid, with a dilute aqueous solution of sodium carbonate, further with water and with mercury for a long time, and finally distilled twice in a long column. A commercial *n*-butyl amine was fractionally distilled twice with sodium in a long column covered with aluminum foil in order to protect the amine from decomposition by light. The gas chromatographs of all the samples on polyethylene glycol and d-nonyl phthalate substrates showed a single peak.

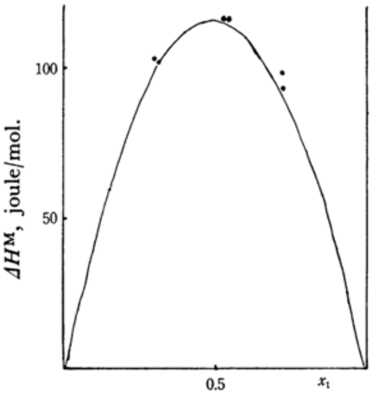

Fig. 2. Heats of mixing curve for carbon tetrachloride+benzene system.
—— Larkin and McGlashan
● This work

Results and Discussion

The measurements of heats of mixing were carried out on the polar liquid+*n*-hexane systems and *n*-butanol+polar liquid systems at 25.0±0.01°C. The results obtained are given in Tables I to VIII and in Figs. 3 to 5, where x_1 is the mole fraction of component 1, and ΔH^{M} and $\Delta H^{\mathrm{M}}_{x_1}$ are the heats of mixing expressed in cal. per mole of mixture and

Table I. Heat of mixing of *n*-butanol (1) and *n*-hexane (2)

Mole fraction of the component 1, x_1	ΔH^{M}, cal./mol. of mixture	$\Delta H^{\mathrm{M}}_{x_1}$, kcal./mol. of the component 1
0.0241	59.2	2.462
0.0543	80.1	1.475
0.1372	115.1	0.840
0.2150	137.6	0.640
0.2803	137.1	0.489
0.2830	143.1	0.506
0.2890	142.2	0.492
0.4765	129.1	0.271
0.4823	130.5	0.271
0.4913	126.1	0.257
0.5863	112.9	0.193
0.7133	85.5	0.120
0.8234	57.0	0.069_3
0.9001	35.9	0.039_8

Table II. Heat of mixing of *n*-butyl ether (1) and *n*-hexane (2)

Mole fraction of the component 1, x_1	ΔH^{M}, cal./mol. of mixture	$\Delta H^{\mathrm{M}}_{x_1}$, kcal./mol. of the component 1
0.0304	2.5_7	0.084_5
0.0366	3.1_8	0.087_0
0.0469	4.2_4	0.090_4
0.0866	8.7_9	0.101
0.0934	11.2	0.117
0.2348	18.7	0.085_2
0.2594	18.5	0.071_3
0.3746	19.3	0.051_4
0.3787	19.0	0.050_3
0.5846	20.2	0.034_6
0.6764	15.9	0.023_5
0.8705	7.8_7	0.009

Table III. Heat of mixing of *n*-butyl amine (1) and *n*-hexane (2)

Mole fraction of the component 1, x_1	ΔH^{M}, cal./mol. of mixture	$\Delta H^{\mathrm{M}}_{x_1}$, kcal./mol. of the component 1
0.0466	54.8	1.176
0.1105	118.1	1.069
0.1613	153.0	0.949
0.2794	215.6	0.772
0.3917	237.6	0.607
0.4905	233.1	0.475
0.6069	225.5	0.372
0.7037	196.4	0.279
0.8197	132.6	0.162
0.8987	80.4	0.089

Table IV. Heat of mixing of acetonitrile (1) and *n*-hexane (2)

Mole fraction of the component 1, x_1	ΔH^{M}, cal./mol. of mixture	$\Delta H^{\mathrm{M}}_{x_1}$, kcal./mol. of the component 1
0.0205	56.4	2.75
0.0236	69.4	2.93
0.0256	57.3	2.24
0.0292	71.5	2.45

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[3] J. A. Larkin and M. L. McGlashan, *J. Chem. Soc.*, **1961**, 3425.

TABLE V. HEAT OF MIXING OF *n*-BUTANOL (1) AND ACETONITRILE (2)

Mole fraction of the component 1, x_1	ΔH^M, cal./mol. of mixture	$\Delta H^M_{x_1}$, kcal./mol. of the component 1
0.0306	64.5	2.105
0.544	107.4	1.975
0.1056	190.5	1.808
0.2065	325.7	1.577
0.2793	381.0	1.364
0.3748	419.6	1.119
0.4906	437.3	0.891
0.4968	437.4	0.881
0.5154	436.2	0.846
0.5708	425.0	0.745
0.7009	360.4	0.514
0.7721	278.5	0.361
0.9067	149.7	0.165

TABLE VI. HEAT OF MIXING OF *n*-BUTANOL (1) AND ACETONE (2)

Mole fraction of the component 1, x_1	ΔH^M, cal./mol. of mixture	$\Delta H^M_{x_1}$, kcal./mol. of the component 1
0.0341	53.4	1.566
0.0599	88.1	1.471
0.1266	163.0	1.288
0.2209	244.5	1.107
0.2486	268.4	1.080
0.3584	305.4	0.852
0.4121	311.9	0.757
0.4841	328.8	0.675
0.4904	326.7	0.666
0.4906	327.5	0.660
0.5475	328.3	0.600
0.6843	297.9	0.435
0.6937	296.5	0.427
0.8086	200.8	0.248
0.8448	180.6	0.214
0.8997	111.4	0.124

TABLE VII. HEAT OF MIXING OF *n*-BUTANOL (1) AND *n*-BUTYL ETHER (2)

Mole fraction of the component 1, x_1	ΔH^M, cal./mol. of mixture	$\Delta H^M_{x_1}$, kcal./mol. of the component 1
0.0202	24.4	1.210
0.0626	70.2	1.121
0.1205	124.4	1.032
0.1627	145.7	0.896
0.2026	175.2	0.865
0.2940	189.4	0.644
0.3828	191.7	0.501
0.4038	191.6	0.480
0.4412	188.9	0.410
0.4741	191.9	0.405
0.5665	172.7	0.305
0.6858	145.5	0.212
0.7901	106.8	0.135
0.9153	42.4	0.045

TABLE VIII. HEAT OF MIXING OF *n*-BUTANOL (1) AND *n*-BUTYL AMINE (2)

Mole fraction of the component, 1, x_1	ΔH^M, cal./mol. of mixture	$\Delta H^M_{x_1}$, kcal./mol. of the component 1
0.0348	65.8	1.891
0.0590	111.7	1.893
0.1013	190.2	1.894
0.1027	197.6	1.923
0.2118	375.5	1.773
0.3013	487.5	1.619
0.3935	566.7	1.440
0.4781	599.6	1.254
0.5848	564.8	0.966
0.6864	497.2	0.724
0.8031	437.1	0.494
0.8910	212.1	0.238

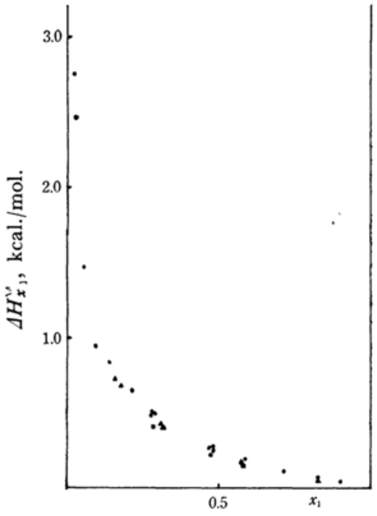

Fig. 3. Heats of mixing for *n*-butanol+*n*-hexane system.
■: Wolf, Pahlke and Wehage
▲: Brown, Fock and Smith
●: This work

those expressed in kcal. per mole of component 1 respectively.

In Fig. 3, the results we obtained for the *n*-butanol+*n*-hexane system are compared with those reported by Brown, Fock and Smith,4) and also those reported by Wolf, Pahlke and Wehage.5) A fairly good agreement is found between the present results and the previously published ones.

Plotting ΔH^M_x against x_1 and extrapolating the curve to an infinite dilution ($x_1 \rightarrow 0$) for each system, as is shown in Figs. 3 to 5, we can obtain the heats of mixing per mole of component 1 at the infinite dilution ($\lim_{x_1 \rightarrow 0} \Delta H^M_x$). They are as follows:

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4) I. Brown, W. Fock and F. Smith, *Aust. J. Chem.*, **17**, 1106 (1964).

5) Landolt-Börnstein, "Physikalishe-Chemischen Tabellen," Springer, Berlin (1936).

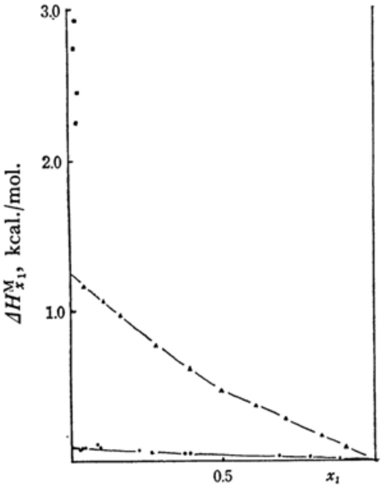

Fig. 4. Heats of mixing for polar liquid+ *n*-hexane system.
■: Acetonitrile+*n*-hexane
▲: *n*-Butyl amine+*n*-hexane
●: *n*-Butyl ether+*n*-hexane

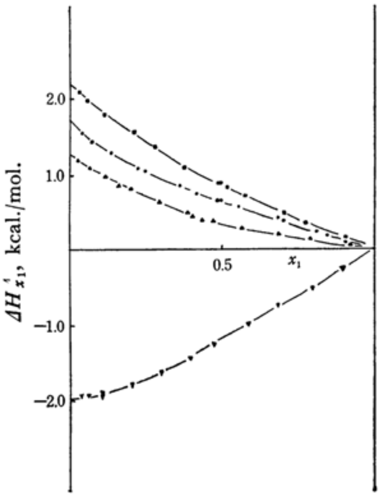

Fig. 5. Heats of mixing for *n*-butanol+polar liquid system.
■: *n*-Butanol+acetonitrile
●: *n*-Butanol+acetone
▲: *n*-Butanol+*n*-butyl ether
▼: *n*-Butanol+*n*-butyl amine

2.25 kcal. for the *n*-butanol(1)+acetonitrile(2)

1.70 kcal. for the *n*-butanol(1)+acetone(2)

1.26 kcal. for the *n*-butanol(1)+*n*-butyl ether(2)

−1.98 kcal. for the *n*-butanol(1)+*n*-butyl amine (2)

1.27 kcal. for the *n*-butyl amine(1)+*n*-hexane(2)

0.10 kcal. for the *n*-butyl ether(1)+*n*-hexane(2)

For the *n*-butanol+*n*-hexane system, as is shown in Fig. 3, however, the extrapolation to $x_1=0$ is very difficult because the curve is very steep at small x_1 values and the measurements are accompanied with considerable errors at these concentration ranges. Fortunately, the value of $\lim_{x_1\to 0}\Delta H^{\mathrm{M}}_{x_1}$ had been found by Pahlke[5] for this system to be 5.50 kcal. Therefore, we have adopted 5.50 kcal. for the $\lim_{x_1\to 0}\Delta H^{\mathrm{M}}_{x_1}$ of this system.

Measurements of the acetonitrile+*n*-hexane system were also very difficult, because only a slight amount of acetonitrile dissolves into *n*-hexane at room temperature. The $\Delta H^{\mathrm{M}}_{x_1}$ values obtained for this system have scattered from 2.2 to 2.9 kcal./mol. at $x_1\simeq 0.02$. The extrapolation to $x_1=0$, using only experimental data in the limited concentration range, gives 3 kcal., but its error may amount to ± 0.5 kcal.

In pure alcohol, all the molecules form hydrogen bonding with each other, while each alcohol molecule in the infinite dilution of alcohol in hexane is surrounded by hexane molecules and the hydrogen bonds are broken. Therefore, the value of 5.50 kcal. represents the energy sufficient to break the hydrogen bonds of pure alcohol. Similarly, the $\lim_{x_1\to 0}\Delta H^{\mathrm{M}}_{x_1}$ values for the alcohol+polar liquid systems correspond to the energy change from the pure alcohol state to that in which each alcohol molecule makes a hydrogen bond with a polar molecule and in which such complexes are surrounded with a large amount of the polar-liquid medium. Roughly speaking, the difference between the $\lim_{x_1\to 0}\Delta H^{\mathrm{M}}_{x_1}$ values for the alcohol + polar liquid systems and that for the alcohol + hexane system may correspond to the measure of the alcohol + polar liquid intermolecular hydrogen bonding. The results are as follows:

−2.25 kcal. for *n*-butanol+acetonitrile

−3.80 kcal. for *n*-butanol+acetone

−4.24 kcal. for *n*-butanol+*n*-butyl ether

−7.48 kcal. for *n*-butanol+*n*-butyl amine

It may be seen from these values that butanol forms the strongest hydrogen bond with *n*-butyl amine, while it forms the weakest hydrogen bond with acetonitrile. Strictly speaking, in the values mentioned above, the dipolar stabilization energy must be included, because alcohol + polar liquid complex molecules are embedded in the polar medium.

In order to estimate the hydrogen bond energy more properly, we carried out the treatment described in previous papers,[1,2] applying the thermochemical cycle depicted in Fig. 6. The intermolecular hydrogen bond energy, ΔH_5, between alcohol and polar-liquid molecules is given by:

$$\Delta H_5 = -\Delta H_1 - x\Delta H_2 + \Delta H_3 + \Delta H_4 \qquad (1)$$

TABLE IX. PHYSICAL CONSTANTS OF ALCOHOL-POLAR LIQUID COMPLEXES NECESSARY FOR CALCULATION OF DIPOLAR ENERGIES AND CALCULATED VALUES OF ΔG_i AND ΔH_i

	μ D	t °C	α $\times 10^{23}$	a^3 $\times 10^{23}$ cc.	$-\Delta G_p$ kcal./mol.	$-\Delta H_p$ kcal./mol.	$-\Delta G_H$ kcal./mol.	$-\Delta H_H$ kcal./mol.
		15	1.3189	5.6793	4.0964		1.3565	
A-CN	5.11	20	1.3192	5.7101	4.0639	5.97	1.3413	2.23
		25	1.3194	5.7414	4.0310	5.99	1.3261	2.23
					Average	5.98	Average	2.23
		15	1.5187	6.5045	2.3106		0.79489	
A-K	4.19	20	1.5192	6.5422	2.2890	3.55	0.78567	1.32
		25	1.5194	6.5794	2.2676	3.55	0.77659	1.32
					Average	3.55	Average	1.32
		15	2.5035	10.295	0.32774		0.19493	
A-E	2.60	20	2.5034	10.344	0.32157	0.68	0.19289	0.313
		25	2.5039	10.399	0.31518	0.70	0.19072	0.319
					Average	0.69	Average	0.32
		15	1.8309	7.5211	0.56774		0.25443	
A-NH_2	2.54	20	1.8282	7.5403	0.55873	1.09	0.25231	0.37
		25	1.8254	7.5598	0.54935	1.11	0.25019	0.37
					Average	1.10	Average	0.37

Dielectric constant;

t°C	15	20	25
Acetonitrile	38.3	37.5	36.7
Acetone	(21.7)	21.2	20.7
n-Butyl ether	(3.18)	(3.12)	3.06
n-Butyl amine	(5.52)	5.34	5.16
n-Hexane	1.897	1.890	1.883

* μ, α and a are dipole moment, the polarizability and the molecular radius of the A-polar liquid complex, respectively. They are estimated in the same way as that described in the previous paper.[1]

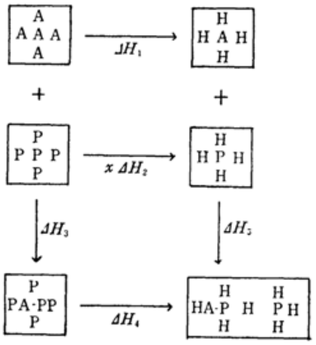

Fig. 6. The thermochemical cycle.

Here ΔH_1 is the energy of breaking the hydrogen bonds of pure alcohol by adding a large quantity of hexane; $x\Delta H_2$, the heat of the dilution of x mol. of polar liquid by a large amount of hexane and ΔH_3, the energy change accompanied by the dilution of the pure alcohol by a large amount of polar liquid; ΔH_4 consists of two parts; the first one is equal to $(x-1)\Delta H_2$, while the second one is due to the difference in the dipolar stabilization energy of a complex dipole arising from the reaction field by different media. This part of the energy change in ΔH_4 may be calculated by the previously-described method.[1,2] The results obtained are summarized in Table IX, together with the data necessary for this calculation.

By using the ΔH_4 value calculated above and the other measured values, the intermolecular hydrogen bond energies between the alcohol and polar molecules, ΔH_5, are found from Eq. 1 to be:

for n-butanol+acetonitrile (A-CN):

$$\Delta H_5 = -5.50 - 3x + 2.25 + 3.75 + 3(x-1)$$
$$= -2.50 \text{ kcal.}$$

for n-butanol+acetone (A-K):

$$\Delta H_5 = -5.50 - 2.15x + 1.70 + 2.23 + 2.15(x-1)$$
$$= -3.72 \text{ kcal.}$$

for n-butanol+n-butyl ether (A-E):

$$\Delta H_5 = -5.50 - 0.10x + 1.26 + 0.37 + 0.10(x-1)$$
$$= -3.97 \text{ kcal.}$$

for n-butanol+n-butyl amine (A-NH_2):

$$\Delta H_5 = -5.50 - 1.27x - 1.98 + 0.72 + 1.27(x-1)$$
$$= -8.03 \text{ kcal.}$$

The strength of the hydrogen bond between alcohol and polar molecules is in the following order:

$$\text{A-NH}_2 > \text{A-E} > \text{A-K} > \text{A-CN}.$$

It is known from the spectroscopic study[6] that the shift in the frequency of the O–H bands, $\Delta\nu_s$, of alcohol in a variety of polar liquids is arranged in the order of:

$$\text{A-NH}_2 > \text{A-E} > \text{A-K} > \text{A-CN}.$$

Therfore, if $\Delta\nu_s$ is correlated with the energy of a hydrogen bond, the above-estimated intermolecular hydrogen bond energies agree with the results obtained from the spectroscopic study.

Summary

The heats of the mixing of *n*-butanol with polar liquids (acetonitrile, acetone, *n*-butyl ether, and *n*-butyl amine) and those of polar liquids with *n*-hexane have been measured calorimetrically. The results obtained for these systems have been compared with one another, and it has been found that the intermolecular hydrogen bond energies between alcohol and polar molecules are as follows:

−2.5 kcal. for *n*-butanol+acetonitrile
−3.7 kcal. for *n*-butanol+acetone
−4.0 kcal. for *n*-butanol+*n*-butyl ether
−8.0 kcal. for *n*-butanol+*n*-butyl amine

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[6] W. Gordy, *J. Chem. Phys.*, **7**, 93 (1939).