Heats of Mixing for Binary Mixtures. II. The 1, 3-Butanediol - Methylethylketone System

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In the previous paper,[1] we measured the heats of mixing of monoalcohol-ketone systems and estimated the value of the hydrogen-bond energy of the type O–H⋯O= to be about 4 kcal.

In order to make a further study of the interaction between alcohol and ketone, we measured the heats of mixing of the 1, 3-butanediol-methylethylketone system, together with those of the ethanol-methylethylketone system, in which an ethanol molecule may be regarded as a monomer of a butanediol molecule.

This paper will describe the results of the measurement and will discuss the existence of the intramolecular hydrogen bond in butanediol.

Experimental

The apparatus used in this study was the one described in the previous paper,[1,2] except for a slight improvement in the calorimeter to make the handling easier. The calorimeter is shown schematically in Fig. 1.

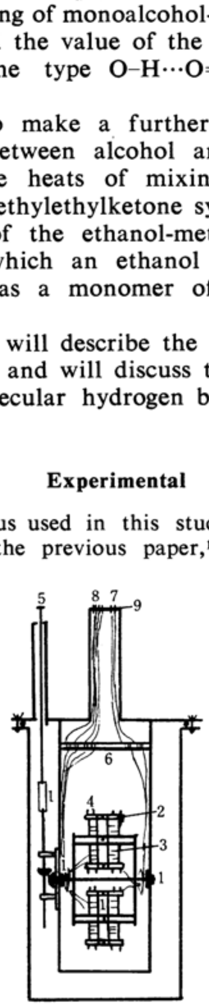

Fig. 1. Calorimeter.

1 Thermal insulater (Teflon)
2 Mixing vessel holder
3 Heater
4 Thermocouple
5 Handle
6 Thermal damper (brass)
7 Lead wire of the thermocouple
8 Lead wire of the heater
9 Harmetic seal

Commercial 1, 3-butanediol was distilled with a Stedman column through nitrogen gas under reduced pressure, and over the molecular sieves in a vaccum. Ethanol and methylethylketone were purified according to the method described in the literature[3] and were finally distilled over the molecular sieves through a long column.

Results and Discussion

The heats absorbed when 1, 3-butanediol and methylethylketone were mixed in various proportions were measured at the temperature of 25.0±0.01°C; the results are shown in Table I, Fig. 2 and Fig. 3. The heats of mixing per mole of solution are shown as

TABLE I. HEATS OF MIXING OF 1, 3-BUTANEDIOL (1) AND METHYLETHYLKETONE (2)

Mole fraction of alcohol (x_1)	ΔH^M cal./mol. of solution	$\Delta H^M_{x_1}$ kcal./mol. of 1
0.0473	80.11	1.69
0.0999	157.4	1.57
0.1363	201.1	1.48
0.1654	239.0	1.44
0.2047	280.3	1.37
0.2126	295.5	1.39
0.2184	291.4	1.33
0.2452	293.5	1.20
0.2855	347.9	1.22
0.3134	367.5	1.17
0.3391	394.4	1.16
0.3418	378.1	1.10
0.4333	383.0	0.884
0.4512	371.5	0.823
0.4522	386.3	0.854
0.4806	370.3	0.770
0.4899	389.6	0.795
0.5217	362.6	0.695
0.5721	364.6	0.637
0.6508	303.8	0.467
0.6527	323.1	0.495
0.7023	281.9	0.401
0.7402	286.0	0.386
0.8295	186.1	0.224

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

[2] K. Amaya and R. Fujishiro, ibid., 34, 1271 (1961).

[3] A. Weissberger and E. S. Porskauer, "Organic Solvents," Interscience Publishers Inc., New York (1955).

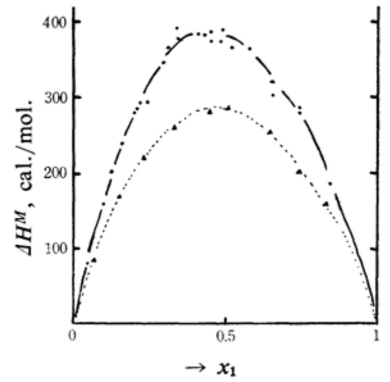

Fig. 2. The plots of ΔH^M vs. mole fraction of alcohol.
—— 1, 3-Butanediol-methylethylketone
...... Ethanol-methylethylketone

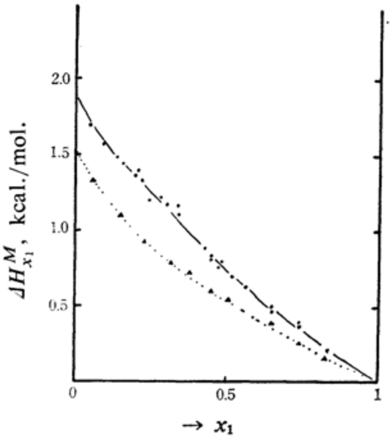

Fig. 3. The plots of $\Delta H^M_{x_1}$ vs. mole fraction of alcohol.
—— 1, 3-Butanediol-methylethylketone
...... Ethanol-methylethylketone

ΔH^M, and those per mole of butanediol as $\Delta H^M_{x_1}$, where x_1 indicates the mole fraction of butanediol. ΔH^M and $\Delta H^M_{x_1}$ versus x_1 are expressed, respectively, by the following equations:

$$\Delta H^M = x_1(1-x_1)\,[1185.8+693.5(1-x_1)]$$

$$\Delta H^M_{x_1} = \Delta H^M/x_1 = (1-x_1)\,[1185.8+693.5(1-x_1)]$$

which are shown by the full lines in Fig. 2 and Fig. 3.

We also measured the heats of mixing of ethanol and methylethylketone in various concentrations at the same temperature; the results are shown in Table II and are depicted by the dotted line in Figs. 2 and 3 against the mole fraction of ethanol. They are expressed by the following equations, which agree well with the experimental data:

TABLE II. HEATS OF MIXING OF ETHANOL (1) AND METHYLETHYLKETONE (2)

Mole fraction of alcohol (x_1)	ΔH^M cal./mol. of solution	$\Delta H^M_{x_1}$ kcal./mol. of 1
0.0636	84.56	1.33
0.1546	169.5	1.10
0.2361	218.1	0.924
0.3340	263.3	0.788
0.3866	280.7	0.726
0.4565	280.2	0.614
0.5083	285.0	0.561
0.6514	254.2	0.390
0.7397	198.3	0.268
0.8150	160.4	0.170

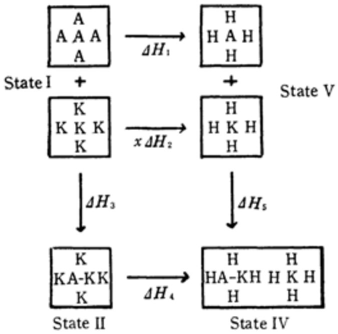

Fig. 4. The thermochemical cycle.

$$\Delta H^M = x_1(1-x_1) \times [1497.2-1673.5(1-x_1)+1698.7(1-x_1)^2]$$

$$\Delta H^M_{x_1} = \Delta H^M/x_1 = (1-x_1) \times [1497.2-1673.5(1-x_1)+1698.7(1-x_1)^2]$$

From these results, the $\lim_{x_1\to 0} \Delta H^M_{x_1}$ values of the butanediol-methylethylketone and ethanol-methylethylketone systems are found to be 1.88 and 1.52 kcal. respectively.

In the previous paper,[1] we estimated the intermolecular hydrogen bond energy of the type O–H···O= for the monoalcohol-ketone system by the use of the following equation, derived from the thermochemical cycle, as in Fig. 4:

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

ΔH_5 is the intermolecular hydrogen-bond energy between alcohol and ketone molecules. ΔH_1 is the energy needed to break the hydrogen bonds of pure alcohol by adding a large quantity of hexane, and $x\Delta H_2$ is the heat of dilution of x moles of ketones by a large amount of hexane. ΔH_3 is the energy of transfer from the pure alcohol state to one in which each alcohol molecule makes a hydrogen bonding with a ketone molecule and in which such complexes are surrounded with a

TABLE III. PHYSICAL CONSTANTS OF ALCOHOL-KETONE COMPLEX NECESSARY FOR THE CALCULATION OF DIPOLAR ENERGIES AND CALCULATED VALUES OF ΔG_i AND ΔH_i FOR THE ETHANOL-METHYLETHYLKETONE SYSTEM

μ D.	t °C	α $\times 10^{23}$	a^3 $\times 10^{23}$ ml.	kcal./mol. ΔG_K		ΔH_K kcal./mol.	ΔG_H kcal./mol.	ΔH_H kcal./mol.
	15	1.3311	5.8293	2.4377			0.8527	
						3.83		1.42
4.11	20	1.3321	5.8648	2.4135			0.8429	
						3.80		1.42
	25	1.3331	5.9010	2.3892			0.8328	
					Av.	3.82		1.42

Dielectric contant t, °C	15	20	25
n-Hexane	1.897	1.890	1.883
Methylethylketone	18.98	18.51	18.07

* μ, α and a are dipole moment, the polarizability and the molecular radius of the alcohol-ketone complex, respectively. They are estimated in the same way as that described in the previous paper (Ref. 1). ΔG and ΔH are the stabilization free energy and the stabilization enthalpy of the complex molecule in the medium. The suffixes K and H represent the media of ketone and hexane, respectively.

large amount of the ketone medium. ΔH_4 consists of two energy changes. The first one is equal to $(x-1)\Delta H_2$. The second one is due to the different dipolar stabilization energies of the dipole of an alcohol-ketone complex arising from the reaction field with different media.

For the ethanol-ketone system, each ΔH_i term ($i=1$, 2, 3 and 4) in Eq. 1 may be estimated as follows. The heat of mixing for monoalcohol-hexane systems was measured and reported by Elbe[4] to be 5.8 kcal. at an infinite dilution, which is adopted as ΔH_1 for ethanol. For ΔH_2, we use 1.90 kcal., as measured in the previous paper.[1] ΔH_3 is 1.52 kcal., which was obtained in this study. The dipolar part of the energy change in ΔH_4 is calculated by the method described in the previous paper.[1] The necessary data in this calculation and the results obtained are summarized in Table III.

By using estimated values of ΔH_1 to ΔH_4 and Eq. 1, ΔH_5 is calculated for the ethanol-methylethylketone system as:

$$\begin{aligned}\Delta H_5 &= -5.80-1.90x+1.52+2.40+1.90(x-1)\\ &= -3.8\ \text{kcal.}\end{aligned}$$

This energy is nearly the same as those derived in the previous paper.[1]

Butanediol is insoluble in any non-polar solvent, and the thermochemical cycle can not be applied to this system. Therefore, we must study the behavior of butanediol from the heats of mixing with ketone. If two hydroxyl groups in a butanediol molecule behave independently of each other, this molecule may be regarded as two ethylalcohol molecules, and the $\lim_{x_1\to 0} \Delta H^M_{x_1}$ value for the butanediol-ketone system may be expected to be twice that for the ethylalcohol-ketone one, that is, $2\times 1.52=3.04$ kcal., because each of these hydroxyl groups has a possibility of making a hydrogen bond with a ketone molecule. However, the actual value of $\lim_{x_1\to 0} \Delta H^M_{x_1}$ for the butanediol system is 1.88 kcal., which is 1.16 kcal. ($=3.04-1.88$) lower than the expected value. This decrease may be ascribed to the interaction of two hydroxyl groups in the butanediol molecule. It is not unreasonable to say that a 1,3-butanediol molecule has so favorable a molecular structure as to make the strong intramolecular hydrogen bond by its two hydroxyl groups, the energy of which may be estimated to be of the same order as that of the intermolecular one. Therefore, if the intramolecular hydrogen bonds are perfectly formed in the ketone medium (an infinitly diluted solution of butanediol in ketone) and are excluded in the pure butanediol state, $\lim_{x_1\to 0} \Delta H^M_{x_1}$ must be 1.52 kcal., and the corresponding decrease of $\lim_{x_1\to 0} \Delta H^M_{x_1}$ from the expected value will also be 1.52 kcal., because upon the perfect formation of intramolecular hydrogen bonds of butanediol in the ketone medium there remains only one hydroxyl group available to form a hydrogen bond with a ketone molecule for each butanediol molecule.

Assuming that there are no intramolecular hydrogen bonds in the pure butanediol state and that the energy of the intramolecular hydrogen bond is nearly the same as that of the intermolecular one, the fraction of the intramolecular hydrogen-bonded form will amount to 80% ($=1.16/1.52$) in the ketone medium.

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[4] G. von Elbe, *J. Chem. Phys.*, **2**, 73 (1934).

In order to confirm the assumption that hardly any intramolecular hydrogen bonds are formed in the pure butanediol, we must estimate the probability that butanediol molecules exist as the intramolecular hydrogen-bonded form. Since a butanediol molecule takes an intramolecular form or an intermolecular one, the probability of the former form is represented in the liquid state of butanediol as:

$$w_{\mathrm{A}}=f_{\mathrm{A}}\exp\left(-E_{\mathrm{A}}/\boldsymbol{RT}\right)/\left[f_{\mathrm{AA}}\exp(-E_{\mathrm{AA}}/\boldsymbol{RT})+f_{\mathrm{A}}\exp\left(-E_{\mathrm{A}}/\boldsymbol{RT}\right)\right] \qquad (2)$$

where f_{A} and f_{AA} are the weights at which the intramolecular and intermolecular forms occur, and E_{A} and E_{AA} are the intra- and inter-hydrogen-bonded energies of alcohol, respectively.

If we replace the butanediol medium which surrounds the butanediol molecule by ketone, we can obtain the state in which the butanediole molecule is surrounded by the ketone medium. This state corresponds to an infinitely dilute solution of butanediol in ketone. In this state, the probability of the intramolecular form is derived in a similar way as:

$$w_{\mathrm{B}}=f_{\mathrm{A}}\exp(-E_{\mathrm{A}}/\boldsymbol{RT})/\left[f_{\mathrm{AK}}\exp(-E_{\mathrm{AK}}/\boldsymbol{RT})+f_{\mathrm{A}}\exp\left(-E_{\mathrm{A}}/\boldsymbol{RT}\right)\right] \qquad (3)$$

where f_{AK} is the weight at which the intermolecular form with a ketone molecule occurs, and E_{AK} is the intermolecular energy between alcohol and ketone molecules. If we tentatively put $E_{\mathrm{A}}=-6$ kcal., $E_{\mathrm{AK}}=-4$ kcal. and $w_{\mathrm{B}}=0.8$ in Eq. 3, we can obtain $f_{\mathrm{AK}}/f_{\mathrm{A}}\simeq 10$. To find w_{A}, we must estimate the order of f_{AA}. Since f_{AA} and f_{AK} are the weights of an intermolecular form in the alcohol and the ketone media respectively, they may not be very different in magnitude. If we put $f_{\mathrm{AA}}/f_{\mathrm{AK}}=2$, that is, $f_{\mathrm{AA}}/f_{\mathrm{A}}\simeq 20$, in Eq. 2, considering that a butanediol molecule has a chance of making more intermolecular hydrogen-bonds (usually twice, as a proton donor and an accepter) in the pure state than in the ketone medium, w_{A} may be estimated to be 5%.

The fact that butanediol liquid is very viscous and insoluble in any non-polar solvent may suggest that strong intermolecular forces act in the liquid state, overcoming the intramolecular forces. Therefore, we may say that, in the pure liquid state of butanediol, the amount of the intramolecular form will be in the range of a few %.

The discussion just mentioned was based on the assumption that the energies of both the inter- and the intra-molecular hydrogen bondings of butanediol are -6 kcal. It may easily be shown that as E_{A} falls off from 6 kcal., the $\lim\limits_{x_1\to 0}\Delta H^M_{x_1}$ value of the butanediol-ketone system must move from 1.52 to 3.04 kcal. The actual value of 1.88 kcal. may indicate that E_{A} is nearly equal to or a little less than E_{AA}.

Consequently, we may conclude that, in the ketone medium, a considerable amount of butanediol molecules or, rather, nearly all the molecules have intramolecular hydrogen-bonded forms, although in the pure state they are hydrogen-bonded with each other.

Summary

The heats of mixing of 1, 3-butanediol and ethanol with methylethylketone have been measured. The results obtained for these two systems have been compared with each other, and it has been found that there exist a considerable number of intramolecular hydrogen bonds of butanediol molecules in the ketone medium.

For the ethanol-methylethylketone system, the energy of the intermolecular hydrogen bond with ketone has been estimated to be about 4 kcal. by using the thermochemical cycle; this value is nearly the same as those obtained for other monoalcohol-ketone systems in the previous paper.[1]

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