Heat of Mixing of Mono- and Di-propylene Glycol with Water

By Kazuo AMAYA and Ryoichi FUJISHIRO*

(Received June 24, 1957)

It will be important to investigate what changes of physical properties of the solutions occur according to the size of the solute molecules. As an attempt we measured the heat of mixing of propylene glycol and di-propylene glycol with water. The di-propylene glycol molecule is thought to be about twice as large as that of propylene glycol; both molecules have the same number of hydroxyl group, but are different in that the former has the ether group.

Measurements of heats of mixing of these solutions, therefore, will give some interesting bits of information about the effect of the molecular size and the interaction power of the ether and the hydroxyl groups with water.

Experimental

The apparatus used was already described in the previous paper[1]. Propylene glycol and di-propylene glycol were distilled with a long column under reduced pressure.

* Present address: Institute of Polytechnics, Osaka City University, Kita-ku, Osaka.

1) K. Amaya and R. Fujishiro, This Bulletin, 29, 270 (1956).

Results and Discussion

The heat which was evolved when propylene glycol (or di-propylene glycol) and water were mixed and then when the solution was diluted successively with propylene glycol (or di-propylene glycol) or water, was measured at 25°C. By integrating these heats evolved by mixing and dilution, the heat of mixing at various concentrations was obtained as shown in Tables I and II. For reference, the heat of mixing and dilution of tri-propylene glycol with water was also measured. But tri-propylene glycol was not distilled because of its high boiling point and so the data may not be reliable enough. Using these data, the heat of mixing per mole of solution was calculated and plotted in Fig. 1.

It will be found that the di-propylene glycol solution shows different and characteristic behavior compared with the propylene glycol solution. One of these behaviors is the shift of the maximum position of the curve to the lower concentration of di-propylene glycol and the other is the increase in the maximum height in the heat of mixing.

Table I
Heat of mixing of propylene glycol and water at 25°C

W. of P.G. g.	W. of water g.	Mole fraction of PG	Heat evolved cal.
1.670	15.649	0.0247	45.9_7
1.670	10.131	0.0376	43.7_1
1.670	6.082	0.0611	39.5_2
1.670	4.018	0.0896	34.7_2
1.670	2.079	0.1598	24.5_2
1.996	2.055	0.1870	27.5_1
4.027	2.055	0.3170	31.8_7
7.958	2.055	0.4784	34.8_3
15.010	2.055	0.6336	37.4_5

Table II
Heats of mixing of di-propylene glycol and water at 25°C

W. of di-PG g.	W. of water g.	Mole fraction of di-PG	Heat evolved cal.
1.991	16.496	0.0160	52.6_2
1.991	8.277	0.0313	46.8_8
1.991	4.178	0.0602	36.0_0
2.058	2.002	0.1213	28.2_0
4.146	2.002	0.2176	30.6_0
8.073	2.002	0.3513	30.7_1
14.813	2.002	0.4984	30.7_4

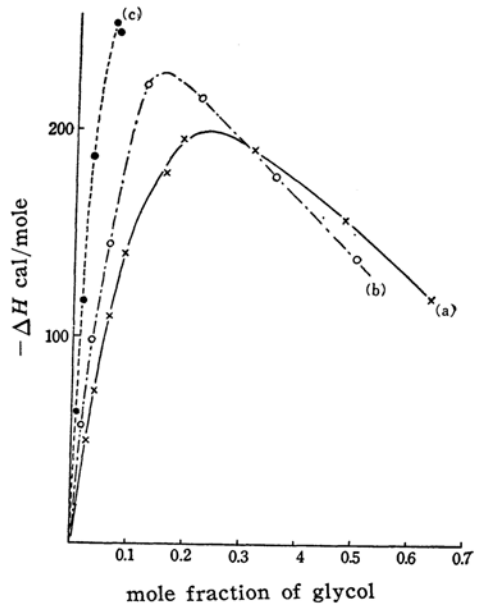

Fig. 1.
(a) Propylene glycol-water
(b) Di-propylene glycol-water
(c) Tri-propylene glycol-water

Usually the heat of mixing per unit volume of the solution of two kinds of normal liquid which have no specially interacting group, may be represented by the following van Laar equation:

$$\Delta H_m/cc = \alpha v(1-v) \qquad (1)$$

where α is the interaction parameter between the solute and the solvent molecules and v is the volume fraction of the solute. According to this equation the position of the maximum of $|\Delta H_m/cc|$ will be at the equi-volume concentration. Assuming that the ratio of molecular volume of the solute to the solvent be n, the heat of mixing per mole of solution will be rewritten as the function of mole fraction x by

$$\Delta H_m/\text{mole} = V_0\alpha x(1-x)/\{1-(n-1)x\}$$

where V_0 is the molar volume of the solvent. Accordingly, the maximum of ΔH_m/mole may be easily calculated to be at $x_{max}=(\sqrt{n}-1)/(n-1)$, which shows that x_{max} decreases as the molecular size of the solute increases.

When one or both liquids have specific groups of interaction, the value of x_{max} will deviate more or less from these normal ones with the degree of interaction, because in such cases the van Laar equation can not be applied owing to the deviation from random mixing.

The propylene glycol-water and the di-propylene glycol-water system which have the effective hydroxyl groups, may be such cases, and the deviation from the normal behavior in both cases is supposed to be considerable.

The ratio n of the molecular volume of propylene glycol or di-propylene glycol to water being 4.1 or 7.2, x_{max} is expected to be 0.33 or 0.27 respectively, which should be compared with the observed value 0.24 or 0.15.

It will not be surprising that both the observed values deviate in similar order from the normal ones and that the observed value of x_{max} for the di-propylene glycol-water system is lower than that for the propylene glycol-water system. It seems strange that the height of the maximum for the di-propylene glycol-water system is higher than that for the propylene glycol-water system, as di-propylene glycol and propylene glycol have the same number of hydroxyl groups which are supposed to show the main interaction with water. But the di-propylene glycol molecule has the oxygen atom making the ether bonding in its center, while the propylene glycol molecule has not. This oxygen atom in the di-propylene glycol molecule may be supposed to play an important role as an acceptor of hydrogen bonding with water, and to make a considerable contribution to the heat of mixing.

This remarkable power of the oxygen atom may be seen in the tri-propylene glycol-water system shown in Fig. 1, in which the former molecule has two such oxygen atoms making the ether bonding.

In order to make a further study of this fact, the heat of mixing per mole of propylene glycol or di-propylene glycol was calculated from the experimental data and plotted against the concentration of propylene glycol or di-propylene glycol in Fig. 2. In the low concentration range, the plots prove to be nearly linear. Extrapolation to the infinite dilution of propylene glycol or di-propylene glycol gives 2.3 kcal. and 4.1 kcal. for the propylene glycol-water solution and the di-propylene glycol solution respectively. This great difference of 1.8 kcal. may be attributed to the existence of the oxygen atom making the ether bonding in the di-propylene glycol molecule.

By considering di-propylene glycol as two unit molecules of propylene glycol, the heat of mixing per unit mole of solution (number of water molecules plus two times number of the di-propylene glycol molecules equal to a mole) was calculated from the experimental data and shown in Fig. 3 with that of the propylene glycol system. It will be seen that the curves for both systems nearly

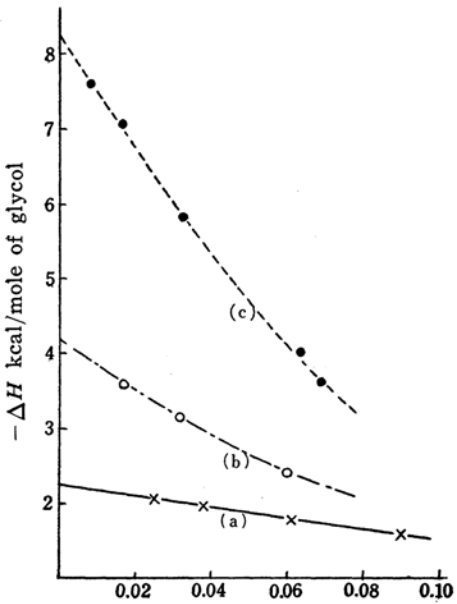

Fig. 2.
(a) Propylene glycol-water
(b) Di-propylene glycol-water
(c) Tri-propylene glycol-water

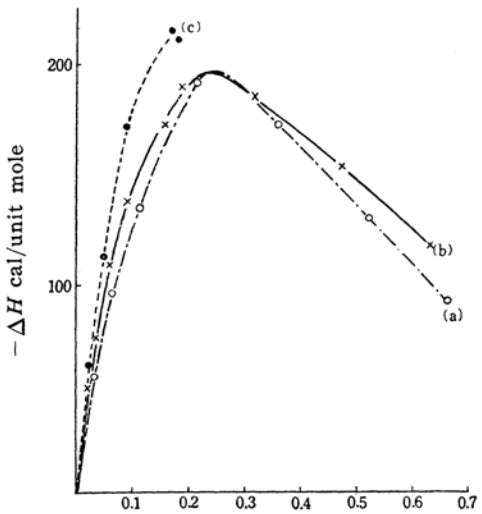

Fig. 3.
(a) Propylene glycol-water
(b) Di-propylene glycol-water
(c) Tri-propylene glycol-water

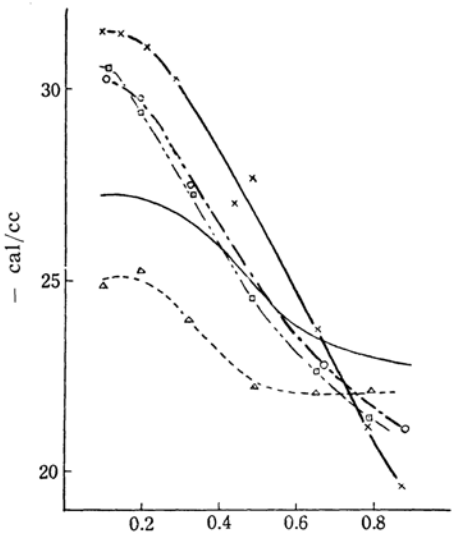

Fig. 4.

—×— Propylenglycol-water
-○- - Di-propylene glycol-water
-◙-·· 1.3-Butanediol-water
—— Ethylene glycol-water
- -△- - 1.4-Butandiol-water

coincide in the height and in the position of the maximum. It may be reasonable to suppose that the di-propylene glycol molecule shows the same behavior as that of two units of a propylene glycol molecule and hence the oxygen atom in the ether bonding has the same power of interaction for water as that of two hydroxyl groups.

Finally, we shall compare the interaction parameter α of our two systems with those of the solutions containing such molecules as ethylene glycol[2] and butanediol[3] which have two hydroxyl groups. Using Eq. (1) the values of α for several systems were calculated and illustrated in Fig. 4. The similar behaviors in cases where the values of α are fairly great in magnitude and decrease considerably as the concentration of diol increases, will be found for all systems shown in Fig. 4 and hence may be characteristic of these solutions in which hydroxyl groups play an important role.

Summary

The heat of mixing of propylene glycol and di-propylene glycol with water was measured. The results obtained for these systems were compared with each other and it was found that the oxygen atom in the ether bond of di-propylene glycol plays an important role for the acceptor of hydrogen bonding and makes a great contribution to the heat of mixing.

We would like to express our gratitude to Professor Y. Morino of Tokyo University for his encouragment and discussion.

Department of Chemistry, Faculty of Science, Kobe University
Higashinada-ku, Kobe

2) Schwers, *Rec. trav. chim.*, **28**, 44 (1909).
3) K. Amaya and R. Fujishiro, This Bulletin, **29**, 830 (1956).