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Temperature Dependence of the Heats of Solution of Poly(ethylene glycol) and of Related Compounds

Haruo NAKAYAMA

Department of Chemistry, Faculty of Engineering, Yokohama National University,
Ooka-machi, Minami-ku, Yokohama

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The heats of solution of poly(ethylene glycol) and of related compounds (1,4-dioxane, tetrahydrofuran, ethylene glycol, diethylene glycol, and several ethyl ethers of ethylene glycol and of diethylene glycol) have been measured as a function of the temperature. The change in the partial molar heat capacity of the solute molecule in the dissolution process, $\Delta\bar{C}_{p2}$, is obtained from the temperature coefficient of the heat of solution. The $\Delta\bar{C}_{p2}$ for poly(ethylene glycol) is 15 cal/deg per $-CH_2CH_2O-$ chain unit. This value is in good agreement with those obtained for other low-molecular-weight compounds. The effect of the polar groups (the ethereal oxygen atom and the hydroxyl group) on the iceberg formation around the nonpolar residues has been discussed. From the results obtained, it seems likely that the iceberg formation around the $-CH_2CH_2O-$ group is somewhat suppressed by the orientation-dependent interactions (hydrogen bond formation) between the ethereal oxygen atom and the water molecule.

As a typical solvent, water has many unique properties which depend on the nature of the molecules dissolved in it. When a compound containing a nonpolar group only (such as hydrocarbon) is introduced into an aqueous solution, an ice-like structure is stabilized in the neighborhood of the solute (the iceberg formation[1)]). On the other hand, in aqueous solutions of substances having not only nonpolar residues, but also functional groups which may participate in hydrogen bonding, the situation becomes much more complex and their thermodynamic functions are apparently governed to a considerable extent by the relative strengths of the two types of interactions: nonpolar group-water (such as the iceberg formation) and polar group-water (such as the hydrogen-bond formation).

In the present investigation, we have been concerned with the aqueous-solution properties of the latter compounds, that is, the molecules having both nonpolar residues and polar groups, in order to ascertain how the hydrogen-bond formation influences the water structure around the nonpolar groups which are located near or adjacent to the functional groups. It is obvious from several investigations[2–6)] that the ions with large nonpolar groups promote the water structure by increasing its likeness to ice. However, so far little is known about the structure-making effect of relatively small nonpolar residues which are directly connected with the functional groups. As a typical example of such a characteristic compound, we have chosen poly(ethylene glycol), in which each ethylene group is hemmed in by ethereal oxygen atoms.

The partial molar heat capacities of solutes in aqueous solutions make them suitable for studying the influence of the solutes on the structural modifications of water.[6)] Therefore, we have determined the change in the heat capacity for the dissolution process by measuring the temperature dependence of the heats of solution. The heats of solution at infinite dilution, ΔH_s°, are simply expressed as:

$$\Delta H_s^\circ = n_2(\bar{H}_2^\circ - H_2), \tag{1}$$

where $\bar{H}_2^\circ$ is the partial molar-heat content of the solute at an infinite dilution, $\bar{H}_2$ is the molar-heat content of the pure solute, and n_2 is the number of moles of the solute. The temperature coefficient of Eq. (1) gives the change in the heat capacity for the dissolution process, $\Delta\bar{C}_{p2}$:

$$\frac{\mathrm{d}(\Delta H_s^\circ)}{\mathrm{d}T} = n_2(\bar{C}_{p2}^\circ - C_{p2}) = n_2\Delta\bar{C}_{p2} \tag{2}$$

in which $\bar{C}_{p2}$ is the partial molar-heat capacity of the solute at an infinite dilution, while C_{p2} is the molar-heat capacity of the pure solute.

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1) H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945).

2) R. L. Kay, T. Vituccio, C. Zawoyski and D. F. Evans, *J. Phys. Chem.*, **70**, 2336 (1966).

3) S. Lindenbaum and G. E. Boyd, *ibid.*, **68**, 911 (1964).

4) W. Y. Wen and S. Saito, *ibid.*, **68**, 2639 (1964).

5) R. L. Ray and D. F. Evans, *ibid.*, **70**, 2325 (1966).

6) S. Subramanian and J. C. Ahluwalia, *ibid.*, **72**, 2525 (1968).

Experimental

Materials. The poly(ethylene glycol) was obtained from the Wako Pure Chemicals Company and was purified by recrystallization from a hot methyl-ethyl ketone solution. The melting point was 61.5—62.3°C, and its molecular weight was about 1.4×10^4, as was estimated from the intrinsic viscosity measurements (0.224 cc/g in water at 25°C). The ethylene glycol, the diethylene glycol, the mono- and di-ethyl ethers of these glycols, the 1,4-dioxane, and the tetrahydrofuran were of a reagent grade and were purified by vacuum distillation just before use. The 1,4-butanediol was of a reagent grade and was used without further purification.

Calorimetric Measurements. The calorimeter employed in this study was a twin-type micro-calorimeter manufactured by Oyodenki Kenkyujo (CM-502).[7] Each sample (about 0.5 g or less), sealed in an ampoule, was dissolved into 50 m*l* of redistilled water whose temperature was kept constant. The measured values of the heat of solution may be in error by as much as 4% at worst. The results shown in Figs. 1 and 2 and tabulated in Table 1 are averages of three or four determinations.

Table 1. Heats of solution and $\Delta\bar{C}_{p2}$'s for PEG and related compounds

Substance	Heat of solution (kcal/mol) 25°C	Heat of solution (kcal/mol) 40°C	$\Delta\bar{C}_{p2}$ (cal/deg·mol)
$-(CH_2CH_2O)_n-$	+0.07	+0.29	15
$(CH_2CH_2O)_2$	−2.58	−2.21	25
CH_2CH_2 $>O$ CH_2CH_2	−3.96	−3.09	58
$HOCH_2CH_2OH$	−1.74	−1.76	0 (0)*
$HOCH_2CH_2OC_2H_5$	−4.38	−4.05	22 (22)
$C_2H_5OCH_2CH_2OC_2H_5$	−6.94	−6.30	43 (44)
$HO(CH_2CH_2O)_2H$	−3.81	−3.58	15 (15)
$HO(CH_2CH_2O)_2C_2H_5$	−6.91	−6.37	36 (37)
$C_2H_5O(CH_2CH_2O)_2C_2H_5$	−9.05	−8.17	59 (59)
$HO(CH_2)_4OH$	−2.53	−2.22	21

* See text.

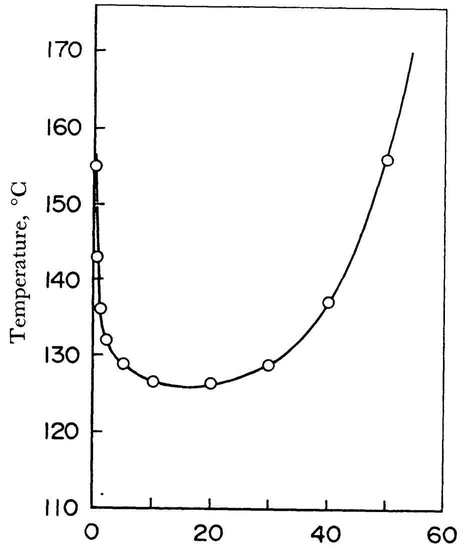

Fig. 1. The liquid-liquid phase diagram for the H_2O-PEG system.

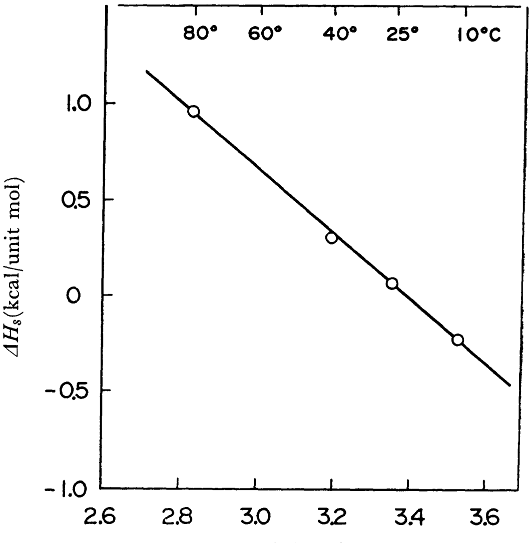

Fig. 2. Temperature dependence of the heats of solution of PEG in H_2O.

Results

The liquid-liquid phase diagram for the water-poly(ethylene glycol) (which we will denote by PEG hereafter) system is shown in Fig. 1. This system has a lower critical solution temperature. The critical solution temperature and critical concentration are about 126°C and 15 wt% respectively. At 160°C, for example, a very dilute solution (less than 0.1%) is in equilibrium with a fairly concentrated solution (*ca.* 50%); the latter corresponds to the solution in which there are 2.5 water molecules per $-CH_2CH_2O-$ group.

The temperature dependence of the heats of solution of solid PEG, ΔH_s, is shown in Fig. 2. The final concentration is about 1%. The heat of solution at 80.3°C (which is higher than the melting point) is obtained by adding the heat of fusion of PEG (2.07 kcal/unit mol[8,9]) to the heat of soultion of liquid PEG at 80.3°C, which has been measured by Rowlinson *et al.*[10] It may be seen from Fig. 2

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[7] K. Amaya, *Bussei*, **4**, 588 (1963); M. Koishi, This Bulletin, **39**, 2406 (1966).

[8] R. H. Beaumont, B. Clegg, G. Gee, J. B. M. Herbert, D. J. Markes, R. C. Roberts and D. Smis, *Polymer*, **7**, 401 (1966).

[9] W. Braun, K.-H. Hellwege and W. Knappe, *Kolloid Z.*, **215**, 10 (1967).

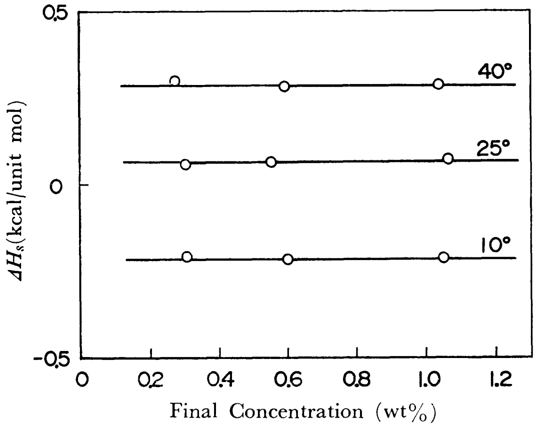

Fig. 3. Concentration dependence of the heats of solution of PEG in H_2O.

that, over the temperature intervals examined, the heat of solution of PEG is approximately a linear function of the reciprocal of the absolute temperature. Obviously, the decrease in exothermicity with rise in the temperature causes phase separation at high temperatures, as is shown in Fig. 1.

In Fig. 3 the concentration dependence of the heats of solution of PEG in dilute regions is shown. As is evident from this figure, the heat of solution is almost independent of the concentration if the final concentration is less than 1%. Therefore, we may safely conclude that the observed heats of solution of PEG (in about a 1% solution, Fig. 2) may be regarded as the heats of solution at an infinite dilution. Thus, from Eq. (2) and Fig. 2, the $\Delta\bar{C}_{p2}$ for PEG can be calculated to be 15 cal/deg. unit-mol around 25°C.

The heats of solution of various low-molecular-weight compounds containing an ethereal oxygen atom and/or a hydroxyl group at 25 and 40°C are listed in Table 1. The final concentration is about 1% or less. For these compounds the values of $\Delta\bar{C}_{p2}$, which are calculated from the temperature coefficients over the 25—40°C temperature range, are also included in Table 1.

Discussion

The heat of solution of solid PEG is slightly endothermic at 25°C (0.07 kcal/unit-mol, as is seen from Fig. 2 or Table 1). This means that the heat of fusion of solid PEG (2.07 kcal/unit-mol[8,9]) is almost canceled out by the exothermic heat of solution of liquid PEG (2.00 kcal/unit-mol). The fact that the introduction of liquid PEG into water leads to a large evolution of heat indicates that the exothermic heat of solution due to a specific interaction between PEG and water exceeds the endothermic heat of solution due to the difference in the cohesive energy densities of the two substances.[11]

The main factors which lead to an exothermic heat of mixing are, presumably: (1) the hydrogen-bond formation between the ethereal oxygen atom of PEG and the hydrogen atom of water, and (2) the structural modifications (the iceberg formation) of water around the hydrocarbon portions of PEG. These interactions will also be reflected in the temperature dependence of the heat of solution. However, we have no quantitative information concerning the effect of the hydrogen-bond formation upon the value of $\Delta\bar{C}_{p2}$. Regarding the latter effect, however, it has been established that the $\Delta\bar{C}_{p2}$ increases about 10 cal/deg·mol[12,13] per $-CH_2-$ group. In any case, we may reasonably expect a value of more than 20 cal/deg-mol for the $\Delta\bar{C}_{p2}$ of the $-CH_2CH_2O-$ group if a stable, ice-like structure is formed in the immediate neighborhood of the $-CH_2CH_2O-$ chain. However, the observed value of $\Delta\bar{C}_{p2}$ for the $-CH_2CH_2O-$ group is 15 cal/deg·mol, as has been mentioned above. This suggests, convincingly but not conclusively, that the iceberg formation around the $-CH_2CH_2O-$ chain is somewhat suppressed by the orientation-dependent interactions (*i. e.*, the hydrogen-bond formation) between ethereal oxygen atoms and water molecules. We believe much more work needs to be done before anything can be said conclusively about the behavior of water molecules in the neighborhood of the $-CH_2CH_2O-$ group.

In Table 1 we may derive some interesting observations about the $\Delta\bar{C}_{p2}$ in relation to the molecular structure:

(1) The $\Delta\bar{C}_{p2}$ for 1,4-dioxane, which is a cyclic dimer of the $-CH_2CH_2O-$ group, is somewhat smaller than twice the $\Delta\bar{C}_{p2}$ for the $-CH_2CH_2O-$ group. On the other hand, for tetrahydrofuran the $\Delta\bar{C}_{p2}$ value is considerably greater than that to be expected from the values of $\Delta\bar{C}_{p2}$ for one $-CH_2CH_2O-$ group and two methylene groups. These discrepancies are probably due to the difference in structure-making ability between the small cyclic molecule and the linear molecule.

(2) The heat of solution of ethylene glycol is almost independent of the temperature around 25°C. This fact suggests that the strong hydrogen-bond formation between the hydroxyl group and the water molecule causes a disruption of the water structure so striking that the structure-making capacity of the methylene group adjacent to the hydroxyl group is considerably lowered. As has

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10) G. N. Malcolm and J. S. Rowlinson, *Trans. Faraday Soc.*, **53**, 921 (1957).

11) K. Shinoda and M. Fujihira, This Bulletin, **41**, 2612 (1968).

12) P. White and G. C. Benson, *J. Phys. Chem.*, **64**, 599 (1960).

13) G. Nemethy and H. A. Scheraga, *J. Chem. Phys.*, **36**, 3401 (1962).

been mentioned above, the occurrence of a similar phenomenon can also be expected in the case of poly (ethylene glycol), though the effect there is not so marked. However, as the $\Delta\bar{C}_{p2}$ of 1,4-butanediol shows (Table 1), the structural modifications of water occur around the methylene groups, remote from the hydroxyl group. An analogous effect has also been observed in the aqueous solutions of alkylhexaoxyethylene glycol monoethers.[14]

(3) The differences in the $\Delta\bar{C}_{p2}$'s between diethylene glycol and ethylene glycol, between diethylene glycol monomethyl ether and ethylene glycol monoethyl ether, and between diethylene glycol diethyl ether and ethylene glycol diethyl ether are 15, 14, and 16 cal/deg·mol respectively. These differences may be ascribed to the cntribution of the $-CH_2CH_2O-$ group to the $\Delta\bar{C}_{p2}$. It is interesting that they are in very good agreement with the $\Delta\bar{C}_{p2}$ observed for the $-CH_2CH_2O-$ group in PEG (15 cal/deg·mol).

(4) If we assign 15 cal/deg·mol to the $\Delta\bar{C}_{p2}$ for the $-CH_2CH_2O-$ group, 22 cal/deg·mol to that for the $-CH_2OC_2H_5$ group, and 0 cal/deg·mol to that for the $-CH_2OH$ group, the $\Delta\bar{C}_{p2}$ values for ethylene glycol, diethylene glycol, and their various ethyl ethers can be reasonably estimated. In Table 1, these calculated values are also listed (in parentheses). They are in good agreement with the observed values.

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[14] J. M. Corkill, J. F. Goodman and J. R. Tate, *Trans. Faraday Soc.*, **63**, 773 (1967).