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Measurements of the Interactions between Polyethylene Glycol and Organic Compounds by Gas Chromatographic Technique*

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A gas-liquid chromatographic technique was employed to measure the thermodynamic properties of the solutions consisting of polyethylene glycol (PEG) and some organic compounds. Three kinds of PEG with different molecular weights were used as a stationary liquid, and six kinds of organic compounds as a solute. For most of the compounds examined, the retention volume varied with the sample size injected. By using the retention volume at an infinitesimal sample size, thermodynamic properties of organic compounds at infinite dilution in PEG, such as the activity coefficient based on weight fraction, Henry coefficient based on weight fraction, and the partial molar excess enthalpy, were determined. From the results it was found that the particular interactions between organic compounds and PEG such as the hydrogen bond formation is not significant, and the solutions can be regarded as a regular solution. The solubility parameters of PEG-600, -1000, and -4000 at 67.3 °C were found to be 10.0, 9.8, and 9.5, respectively.

Many investigations[1)] have been carried out to measure thermodynamic properties of solution with gas-liquid chromatography (GLC). As an example, Everett and Stoddart[2)] measured the infinite dilution activity coefficients of a series of hydrocarbons in dinonyl phthalate by GLC and obtained results in good agreement with those by a static method. However, the technique was not applied to the polymer–organic compound systems until quite recently. Since there exists a distribution of molecular weights in polymer, the activity coefficient based on mole fraction is not adequate for such a system.

Recently the activity coefficients based on weight fraction and molality were proposed for a polymer–organic compound system by Patterson *et al.*,[3)] and Fritz and Kovats,[4)] respectively. On the other hand, Newman and Prausnitz[5)] used the GLC technique to obtain the volatility (based on weight fraction) of solvents in polymer coatings.

In the present work, the measurement of thermodynamic properties based on weight fraction by GLC technique was carried out for the system of polyethylene glycol (PEG) and some organic compounds. PEG is a popular column packing material in gas chromatography, several investigations having been made on its gas chromatographic properties. Adlard[6)] found that the retention volume of alcohol decreases with increase in the molecular weight of PEG. The behavior of alcohol, which is opposite to that of other organic compounds, was considered to be due to hydrogen bond with PEG. Watanabe *et al.*,[7)] and Yamao[8)] independently found a similar behavior for formaldehyde. However, no thermodynamic properties were determined for the reason described above. In this work, the activity coefficient based on weight fraction at infinite dilution, Henry coefficient based on weight fraction, and the partial molar excess enthalpy of mixing were determined for several organic compounds. The solubility parameters of PEG were determined by the method of Takamiya *et al.*[9)] The peculiar behavior of alcohol as regards the retention volume on the molecular weight of PEG could be interpreted by the solubility parameter.

Theoretical

The net retention volume V_N can be related to the partition coefficient K_d for GLC by

$$V_N = K_d V_2 \tag{1}$$

where V_2 is the total volume of stationary liquid in the column. The corrected retention volume divided by the weight of stationary liquid w_2 and converted into 0 °C is called the specific retention volume V_g, which is related to V_N by

$$V_g = \frac{V_N}{w_2}\frac{273}{T_c} \tag{2}$$

where T_c is the column temperature. From Eqs. 1 and 2 we obtain

$$K_d = V_g \frac{w_2}{V_2}\frac{T_c}{273} = V_g \rho_2 \frac{T_c}{273} \tag{3}$$

where ρ_2 is the density of stationary liquid. The value of V_g can be obtained experimentally by means of the equation

$$V_g = \frac{3}{2}\left\{\frac{(p_i/p_o)^2-1}{(p_i/p_o)^3-1}\right\}\frac{273}{T_r}\frac{1}{w_2}t_R F \tag{4}$$

where p_i and p_o are the pressures at inlet and outlet, respectively, t_R is the peak maximum retention time, and F is the flow rate of carrier gas at room temperature T_r.

If the temperature dependence of ρ_2 can be neglected, the differentiation of Eq. 3 by $1/T_c$ gives

$$\frac{d \ln K_d}{d(1/T_c)} = -\frac{\Delta H_s}{R} = \frac{d \ln V_g}{d(1/T_c)} - T_c \tag{5}$$

where ΔH_s is the heat of solution. Thus the value of ΔH_s can be determined from the temperature dependence of V_g.

Following Patterson *et al.*,[3)] the infinite dilution activity coefficient $\gamma_1^\infty(w)$ based on weight fraction is expressed as

$$\ln \gamma_1^\infty(w) = \ln \frac{273R}{M_1 p_1^\circ V_g} - \frac{B_{11}-v_1^\circ}{RT_c}p_1^\circ \tag{6}$$

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TABLE 1. SECOND VIRIAL COEFFICIENTS, VAPOR PRESSURES, AND MOLAR VOLUMES OF SOLUTES AT 67.3 °C

Solute	$-B_{11}$ ml mol^{-1}	p_1° Torr	v_1° ml mol^{-1}
Ethanol	604	486	62.3
Methanol	475	839	43.4
Ethyl acetate	1052	549	104.3
Dichloromethane	611	1852	68.1
Benzene	1041	500	94.1
Hexane	1209	728	140.1

where the subscript 1 denotes the solute. The second term of the right side is a correction for the nonideality of gas phase. B_{11} is the second virial coefficient of pure solute, p_1° the saturated vapor pressure, v_1° the molar volume at column temperature, and M_1 the molecular weight. When B_{11}, p_1°, and v_1° are known, $\gamma_1^\infty(w)$ can be calculated from V_g. In the present work, B_{11} and p_1° were evaluated by the Berthelot relation and the Antoine equation, respectively, the value of v_1° being estimated from the density by using the expansion factor proposed by Watson. These values are given in Table 1.

From the temperature dependence of activity coefficient, the partial molar excess enthalpy of mixing at infinite dilution $\Delta\bar{H}_1^{E\infty}$ can be evaluated by the equation

$$\frac{d\ln\gamma_1^\infty(w)}{d(1/T_c)} = \frac{\Delta\bar{H}_1^{E\infty}}{R}, \tag{7}$$

and the Henry coefficient based on weight fraction H_1 (w) can be evaluated by the equation

$$H_1(w) = p_1^\circ\gamma_1^\infty(w). \tag{8}$$

The solubility parameter of stationary liquid can be determined as follows.

If the temperature dependence of gas phase imperfection term (the second term of right side of Eq. 6) can be neglected, differentiating Eq. 6 by $1/T_c$, and using the relations of Eqs. 5 and 7 and the Clausius-Clapeyron equation, $-d\ln p_1^\circ/d(1/T)=\Delta H_1^v/R$, we obtain[10]

$$-\Delta H_s = \Delta H_1^v - RT_c - \Delta\bar{H}_1^{E\infty} \tag{9}$$

where ΔH_1^v is the heat of vaporization.

The partial molar excess enthalpy in an infinitely dilute regular solution is expressed as

$$\Delta\bar{H}_1^{E\infty} = v_1^\circ(\delta_1-\delta_2)^2 \tag{10}$$

where δ_1 and δ_2 are the solubility parameter of solute and solvent (stationary liquid), respectively. The solubility parameter of solute can be estimated by the equation

$$\delta_1 = \left(\frac{\Delta H_1^v - RT}{v_1^\circ}\right)^{1/2}. \tag{11}$$

Substitution of Eqs. 10 and 11 into Eq. 9 gives

$$-\Delta H_s/v_1^\circ = 2\delta_1\delta_2 - \delta_1^2 \tag{12}$$

which shows that there is a linear relationship between $-\Delta H_s/v_1^\circ$ and δ_1. Hence, if the plot of $-\Delta H_s/v_1^\circ$ against δ_1 is linear, the system can be regarded as a regular solution and δ_2 can be obtained from the slope and also from the intercept, independently.[9]

In the present work, ΔH_1^v was estimated from the slope of the Othmer chart drawn by the vapor pressure data, and δ_1 was calculated from Eq. 11.

Experimental

Apparatus. A Yanagimoto G-80 gas chromatograph was used. The column was a copper tube of 3 mm i.d. and 2 m in length. The measurements were carried out in the range 56.5—77.1 °C. Helium was used as carrier gas. The flow rate was measured at the outlet by soap-film flowmeter and corrected for a vapor pressure of water. The flow rate was kept at 20 ml/min. The sample was injected with a 1-μl micrometer syringe and the sample size was varied below 0.1 μl. The accurate sample size was determined from the peak area in chromatogram.

Stationary Phase and Column Preparation. PEG-600, -1000, and -4000 (Gasukuro Kogyo Co.) were coated on the solid support, 60—80 mesh of Uniport B (Gasukuro Kogyo Co.) in the range of coverage ratio 0.1—0.3. The coverage ratio which was measured with the Soxhlet extractor did not change throughout the measurement.

The properties of PEG used are given in Table 2. The melting range was determined by DSC and the concentration of end hydroxyl group C_{OH} was measured by titration. The average molecular weight M_n was calculated from C_{OH}.

TABLE 2. PROPERTIES OF PEG USED

	C_{OH} mmol g-packing^{-1}	M_n	melt. range °C
PEG-600	3.18	670	−4—17
PEG-1000	1.52	1400	22—48
PEG-4000	0.61	3400	50—59

Solute. The following compounds were used as a solute: ethanol, methanol, ethyl acetate, dichloromethane, benzene, and hexane. They were of reagent grade and used without further treatment.

Preliminary Experiments

Effect of Sample Size on Retention Volume. For most of the solutes, especially for methanol and hexane, the specific retention volume increased with a decrease in the sample size injected. An illustration is given in Fig. 1. The retention volume at the infinitesimal sample size obtained by extrapolation was used for calculation below.

Effect of Coverage Ratio on Retention Volume. In some GLC systems, surface adsorption occurs in addition to absorption. Martin[11] proposed that the retention volume observed would be presented by the sum of two terms,

$$V_R = K_d V_2 + K_a A$$

where K_a is the adsorption coefficient and A is the surface area of stationary liquid. Assuming that A is independent of coverage ratio α and equal to the surface area of solid support, and using V_g instead of V_R, we obtain

$$V_g = \frac{273}{T_c}\frac{1}{\rho_2}K_d + \frac{273}{T_c}s\frac{1-\alpha}{\alpha}K_a$$

where s is the specific surface area of support. Therefore, when there exists a contribution of surface adsorption, V_g should vary with α.

The retention volumes were measured by varying the coverage ratio from 0.1 to 0.3. The result is shown in Fig. 2.

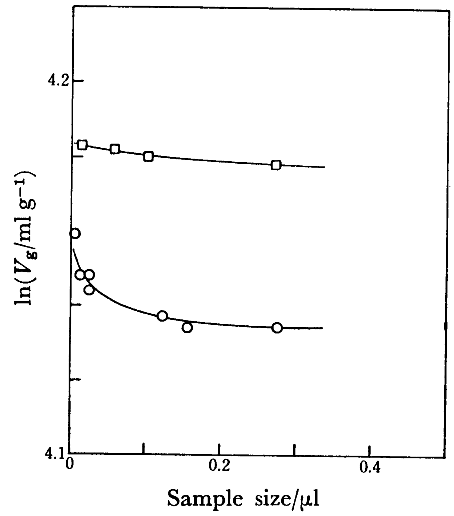

Fig. 1. An example of the variation of specific retention volumes with sample size.
□: Ethyl acetate-PEG-600 at 67.3 °C
○: Methanol-PEG-1000 at 77.1 °C

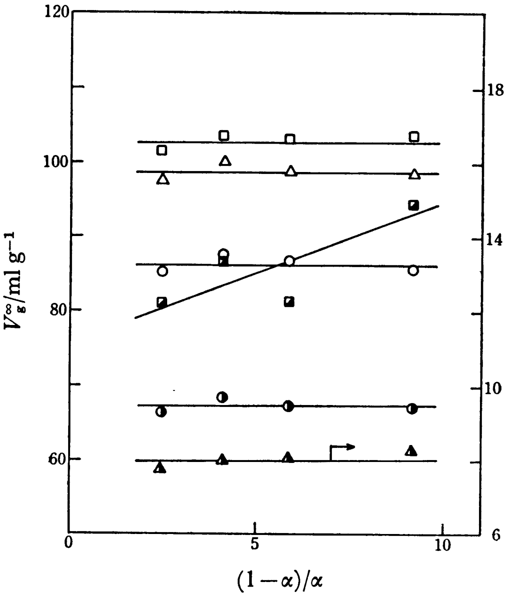

Fig. 2. The plots of V_g^∞ at 67.3 °C *vs.* $(1-\alpha)/\alpha$.
□: Ethanol, ◩: methanol, ◑: ethyl acetate, ○: dichloromethane, △: benzene, ▲: hexane.
The measure of right side is for hexane and the left for others.

Clearly the specific retention volumes are almost constant for more than 0.15 of α except for methanol. Thus the coverage ratio was kept 0.15 for each PEG, and methanol was removed from the discussion below.

Results

Thermodynamic Properties. The infinite dilution activity coefficients and Henry coefficients based on weight fraction are given in Table 3.

The partial molar heats of mixing at infinite dilution were evaluated from the slope of the plot of $\ln \gamma_1^\infty(w)$ against $1/T_c$ according to Eq. 7. An example is shown in Fig. 3.

Variations of Henry coefficients and the partial molar excess enthalpies with the concentration of hydroxyl group of PEG are shown in Figs. 4 and 5, respectively. We see that $\Delta\bar{H}_1^{E\infty}$ and $H_1(w)$ for hexane is much larger than that of other solutes. In the case of ethanol, on the other hand, the dependence of $\Delta\bar{H}_1^{E\infty}$ and $H_1(w)$ on C_{OH} is opposite that of other solutes in agreement with the result of Adlard.

Solubility Parameter of PEG. Adaptability of the thermodynamic properties we obtained to the regular solution theory will be examined. Figure

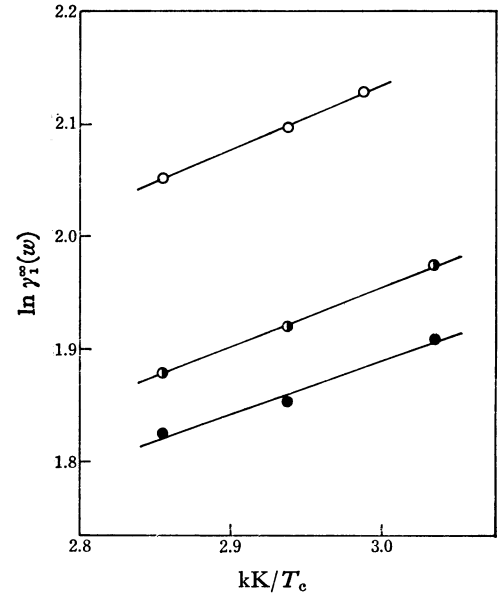

Fig. 3. An example of the plot of $\ln \gamma_1^\infty(w)$ *vs.* $1/T_c$ (sample: ethanol)
●: PEG-600, ◑: PEG-1000, ○: PEG-4000.

TABLE 3. INFINITE DILUTION ACTIVITY COEFFICIENTS AND HENRY COEFFICIENTS BASED ON WEIGHT FRACTION AT 67.3 °C

Solute	$\gamma_1^\infty(w)$ PEG			$H_1(w)/\text{kg atm mol}^{-1}$ PEG		
	-600	-1000	-4000	-600	-1000	-4000
Ethanol	6.39	7.48	8.16	4.09	4.79	5.21
Ethyl acetate	5.53	5.41	5.20	3.99	3.90	3.76
Dichloromethane	1.46	1.33	1.23	3.56	3.23	3.01
Benzene	5.08	4.54	4.24	3.34	2.99	2.79
Hexane	40.1	35.3	32.7	38.4	33.8	31.3

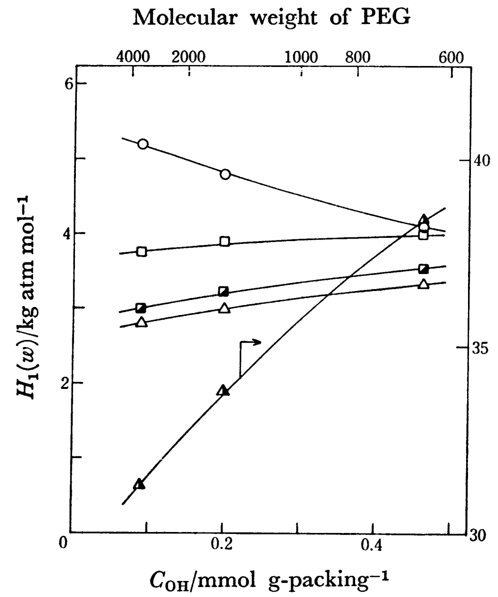

Fig. 4. The effect of end OH group of PEG on Henry coefficient at 67.3 °C.
○: Ethanol, □: ethyl acetate, △: benzene, ◪: dichloromethane, ▲: hexane.
The measure of right side is for hexane and the left for others.

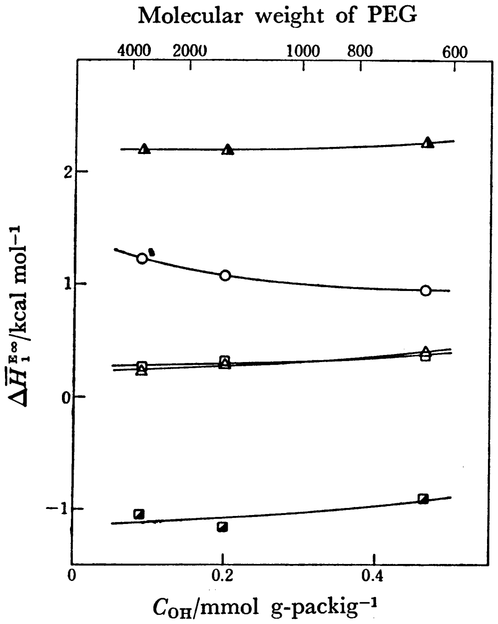

Fig. 5. The effect of end OH group of PEG on partial molar excess enthalpy.
○: Ethanol, □: ethyl acetate, △: benzene, ◪: dichloromethane, ▲: hexane.

6 shows the plot of Eq. 12. There seems to be an excellently linear relationship. The straight lines are computed by least squares treatment of data of all solutes except for the one of dichloromethane which deviates a great deal. The partial molar enthalpy of dichloromethane is negative (exothermic). This is inconsistent with Eq. 10, which shows that $\Delta\overline{H}_1^{E\infty}$ is never negative in a regular solution. Since dichloromethane is electron attractive, this seems to be due to an interaction of charge-transfer type. Therefore,

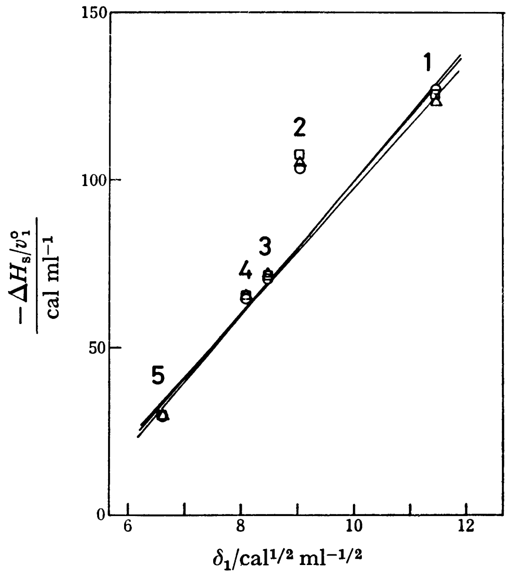

Fig. 6. The plots of $-\Delta H_s/v_1^\circ$ vs. δ_1.
○: PEG-600, □: PEG-1000, △: PEG-4000.
Solute 1: ethanol, 2: dichloromethane, 3: benzene, 4: ethyl acetate, 5: hexane.

the system would not show the behavior of a regular solution.

Solubility parameters of PEG calculated from the plot of Fig. 6 are given in Table 4. The values from the slope and intercept, obtained independently, show good agreement with each other. The solubility parameter decreases with increase in the molecular weight. The value calculated by Small's method[12] is about 9.1 at 25 °C, which may be more small at the measurement temperature. This method, however, refers to high molecular weight polymer in which the contribution of the end group can be neglected.

TABLE 4. SOLUBILITY PARAMETERS OF PEG AT 67.3 °C

	PEG		
	-600	-1000	-4000
From the slope	10.0	9.7	9.4
From the intercept	10.0	9.8	9.5

The hydroxylic compounds usually have high δ values due to self-association. Thus, the values obtained experimentally seem to be reasonable by taking account of the relatively low molecular weight of 600—4000 and of the appreciable contribution of the end hydroxyl group. The order of magnitude of δ is considered to be appropriate since the effect of the hydroxyl group will decrease with increase in molecular weight.

Takamiya et al.[9] obtained values of 8.8 and 10.0 for δ of PEG-400 and -1500, respectively, at 100 °C. While the values are close to our results, δ increases with the molecular weight of PEG. The difference may arise from the error due to a large sample size injected or from the difference in organic compounds used as solutes.

Discussion

Organic solvents can be classified on the basis of potentialities for forming hydrogen bonds.[13] For example, ethanol and methanol belong to the class containing both active donor and acceptor atoms. Benzene is known to be electron donative. Of all the solvents used here only hexane has no active atoms.

On the other hand, PEG has ether groups and end hydroxyl groups. As the molecular weight of PEG becomes larger, its nature as an ether will become dominant. PEG is known to be a polar liquid, and the interaction between PEG and polar solvent is expected to be complicated.

Adlard[6] considered that the different behavior of alcohol from other compounds in the dependence of retention volumes on molecular weight of PEG may arise from the formation of hydrogen bond between alcohols and PEG. It seems to be necessary, however, to take account of the effect of self-association in the case of hydroxylic compounds. We see that $\Delta H_1^{E\infty}$ for ethanol is endothermic (Fig. 5). This suggests that the rupture of self-association of alcohol at infinite dilution will play an important roll as well as the formation of hydrogen bond between PEG and alcohol. These phenomena contribute to the heat of mixing conversely each other. Consequently, the influence of the hydrogen bond on $\Delta H_1^{H\infty}$ will not appear apparently. For other polar compounds except for dichloromethane, no particular interaction is observed.

The system might be treated as a regular solution provided that the influence of a particular interaction such as hydrogen bond would be negligible. In the regular solution theory the heat of mixing is proportional to the difference in solubility parameters between solute and solvent as shown by Eq. 10. The solubility parameter of PEG decreases with increase in its molecular weight. Therefore, the solubility of a compound whose solubility parameter is smaller than that of PEG will increase with the molecular weight of PEG, and a compound of larger parameter than PEG will show the opposite tendency. Among the compounds examined here, only ethanol takes a larger value of solubility parameter than PEG. Thus the peculiar behavior of ethanol against the molecular weight of PEG could be explained in terms of solubility parameter. While particular interactions such as hydrogen bond between PEG and organic compound were expected to exist, the influence of such interactions was negligibly small except for dichloromethane and the solution could be treated as a regular solution.

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