

Thermodynamic Data for Complexes of Triethylamine with Diols in Dichloroethane

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The reactions of triethylamine with hexane-1,6-diol and octane-1,6-diol in dichloroethane were investigated. Both hydroxy groups in the diols are found to be equally reactive with triethylamine. Stability constants and the ΔH° , ΔG° , and ΔS° values for the reactions of triethylamine with the hydroxy groups were determined.

The mechanism of a low-temperature polycondensation process was investigated in our previous paper.¹ This process takes place in the presence of tertiary amines. In order to elucidate the role of tertiary amines in this process, the formation of complexes of triethylamine with bisphenols was investigated. Both hydroxy groups in the bisphenols were found to be equally reactive with triethylamine. Stability constants, rate constants, and the ΔH° , ΔG° , and ΔS° values for the reaction of triethylamine with hydroxy groups were determined. So it seemed to be interesting to check whether the reaction of triethylamine with aliphatic diols occurs, and to determine the stability constants and the ΔH° , ΔG° , and ΔS° values. Since aliphatic alcohols and triethylamine form hydrogen-bond complexes,² one could expect that aliphatic diols and triethylamine should form such complexes as well. In order to investigate this possibility calorimetric and i.r. spectroscopic methods, widely used for studies of complex formation,^{3,4} were chosen.

Experimental

Compounds.—Hexane-1,6-diol was purified by two-fold crystallization in hexane, m.p. 42 °C. Octane-1,8-diol was purified by double crystallization in ether, m.p. 63 °C. M.p.s were determined with a Boëtius apparatus. Triethylamine was purified by the reaction with thionyl chloride and distillation over metallic sodium, b.p. 89 °C. Dichloroethane was purified by washing with a solution of potassium hydroxide and with water, dried and distilled over phosphorus pentoxide, b.p. 83 °C.

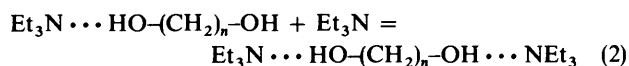
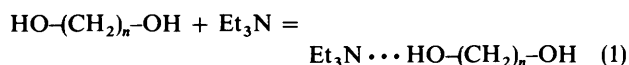
Spectroscopic Measurements.—The i.r. spectra were recorded with a UR-10 (Zeiss, Jena) i.r. spectrophotometer. Absorption measurements of diol solutions with triethylamine were carried out at 28 °C and under a pressure of one atmosphere. Dichloroethane was used as solvent.

Calorimetric Measurements.—Measurements were made in a Calvet-type calorimeter.¹ The measuring cell contained a solution of the studied diol in dichloroethane, a carefully weighed amount of triethylamine being placed in a sealed phial. The reaction started on breaking the phial, the heat evolved being recorded as a thermogram.

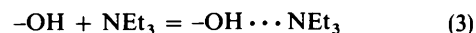
Results and Discussion

The initial diol has two identical hydroxy groups. Thus after one of them has been bonded the other group can also react with a second molecule of triethylamine. Thus, the same molecule of

diol can take part in reactions (1) and (2). Therefore we decided



to relate the thermodynamic data to the reaction of the complex formation by only one hydroxy group, *i.e.* reaction (3). But first



we had to determine whether the reactivity of the other group remained unchanged after one of these groups had been bonded. For this purpose an i.r. spectroscopic method was applied.

Four types of solutions were taken into consideration. The first contained only the diol in dichloroethane. In the second there was a large excess of triethylamine and deficiency of diol, while in the third it was the other way round. The fourth type was an equimolar concentration of triethylamine and hydroxy groups. The typical i.r. absorption spectra obtained are shown in Figures 1 and 2. It seems that the experiments carried out in the presence of a large excess of diol should mostly lead to reaction (1), *i.e.* to complex formation by only one hydroxy group of the diol. And experiments performed with a large excess of triethylamine would lead to the formation of complexes by both hydroxy groups, *i.e.* to reactions (1) and (2). From the curves in Figures 1 and 2 it follows that the position of the maximum absorption corresponding to the complex formed by triethylamine and the hydroxy group is the same for each of the studied types of solutions. The values of the shift of wave number is equal for both diols and amounts to 440 cm^{-1} . From the above it follows that the energy of the hydrogen bond is the same for both groups.⁵ Hence, we can assume identical reactivity for both groups. It was thus possible to relate the equilibrium constants to reaction (3).

The spectrophotometric curves for all types of solutions clearly exhibit the absorption band corresponding to the associated hydroxy groups. That is why the effect of self-association cannot be neglected. We tried to consider the correlation between the concentration of the hydroxy groups of dissolved diol and free hydroxy groups in solution. In order to do that the absorption coefficients for free and associated hydroxy groups were assumed to be equal. Support for this assumption comes from ref. 6. So we can write equations (4)—(6) where A_f and A_b are the absorbance due to free and associated hydroxy groups, respectively, c_f and c_b are the

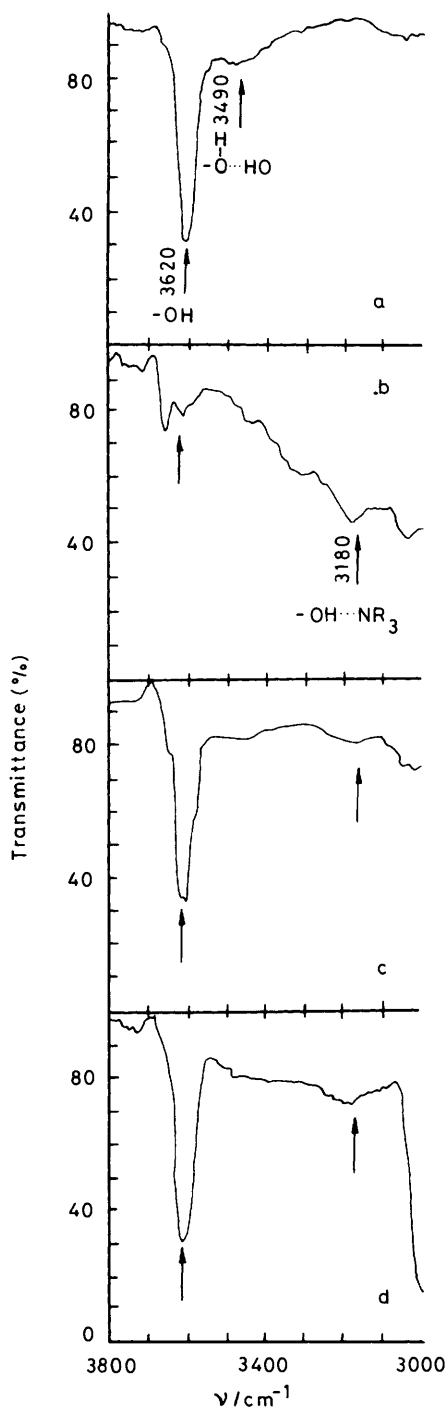


Figure 1. I.r. spectra of hexane-1,6-diol and triethylamine solutions in dichloroethane: a, 0.19 mol dm⁻³ hydroxy groups; b, 0.03 mol dm⁻³ hydroxy groups and 0.21 mol dm⁻³ triethylamine; c, 0.18 mol dm⁻³ hydroxy groups and 0.02 mol dm⁻³ triethylamine; d, 0.17 mol dm⁻³ hydroxy groups and 0.17 mol dm⁻³ triethylamine

$$A_f = a \cdot c_f \cdot l \quad (4)$$

$$A_b = a \cdot c_b \cdot l \quad (5)$$

$$c = c_f + c_b \quad (6)$$

concentration of free and associated hydroxy groups, respectively, and l is the optical path length. From these equations (7)

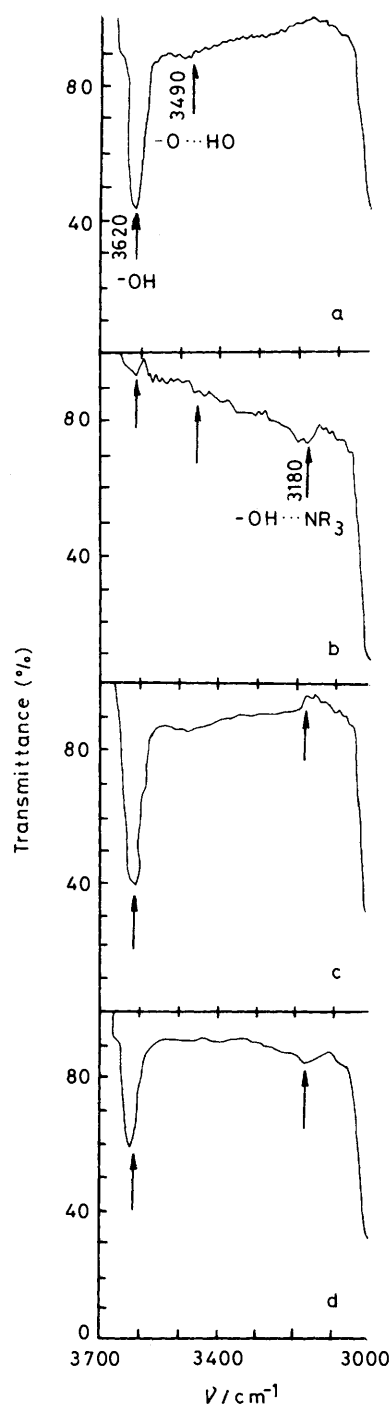


Figure 2. I.r. spectra of octane-1,8-diol and triethylamine solutions in dichloroethane: a, 0.15 mol dm⁻³ hydroxy groups; b, 0.02 mol dm⁻³ hydroxy groups and 0.26 mol dm⁻³ triethylamine; c, 0.13 mol dm⁻³ hydroxy groups and 0.01 mol dm⁻³ triethylamine; d, 0.07 mol dm⁻³ hydroxy groups and 0.07 mol dm⁻³ triethylamine

$$c_f = \frac{c}{1 + \frac{A_b}{A_f}} \quad (7)$$

follows. In order to plot this relation a series of solutions of the first type were studied. The results of measurements are shown in Figure 3. The values of the absorbances were calculated

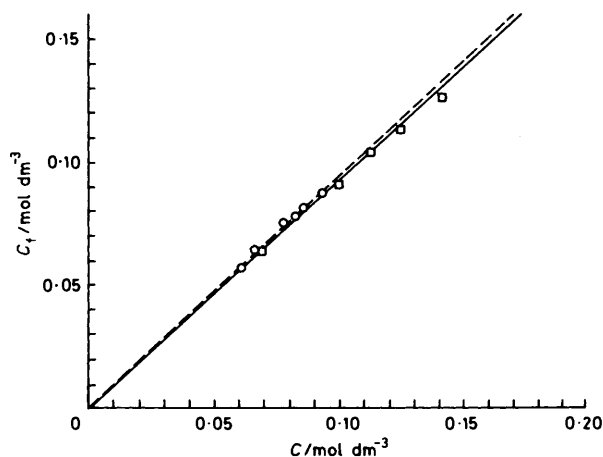


Figure 3. Plot of c_f versus c , \square hexane-1,6-diol; \circ octane-1,8-diol

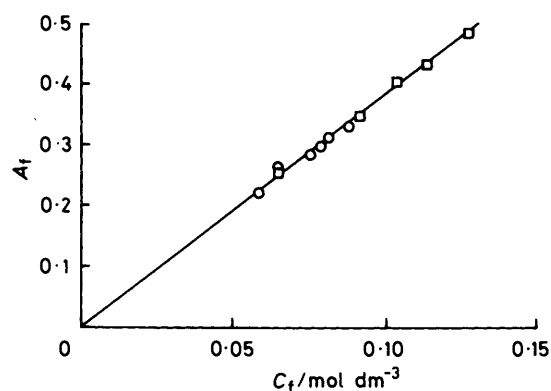


Figure 4. The plot A_f versus c_f , \square hexane-1,6-diol; \circ octane-1,8-diol

directly from the band maxima. In Figure 4 there is a plot A_f as a function of c_f .

For both diols the same straight line through the origin was obtained. Thus Beer's law for A_f and c_f holds.

The equal reactivity of both hydroxy groups in the diols investigated allowed calculations of the equilibrium constants of their reactions with triethylamine. As in other methods applied to investigating the hydrogen-bond complexes in non-electrolyte solution, it was assumed that the activity coefficients were equal to unity.⁷ Thus the equilibrium constant is equation (8) where $c_{\text{OH}\dots\text{N}}$ is the concentration of the formed hydrogen

$$K = c_{\text{OH}\dots\text{N}}/c_{\text{OH}} \cdot c_{\text{Et}_3\text{N}} \quad (8)$$

bond and c_{OH} and $c_{\text{Et}_3\text{N}}$ are the equilibrium concentrations of hydroxy groups and triethylamine, respectively. The values of the equilibrium constants were calculated from a series of measurements on solutions of the fourth type. The concentrations of the formed hydrogen bonds were calculated from the formula $c_{\text{OH}\dots\text{N}} = c_f^\circ - c_f$ where c_f° is the initial concentration of free hydroxy groups taken from the plot of $c_f = f(c)$ in Figure 3; $c_f = c_{\text{OH}}$ is the concentration of free hydroxy groups in equilibrium taken from the plot of $A_f = f(c_f)$ in Figure 4. A_f is the absorbance of the free hydroxy groups calculated on the absorption spectrum of the studied diol. The concentration of the free triethylamine in equilibrium was calculated from the equation $c_{\text{Et}_3\text{N}} = c_{\text{Et}_3\text{N}}^\circ - c_{\text{OH}\dots\text{N}}$ where $c_{\text{Et}_3\text{N}}^\circ$ is the initial concentration of triethylamine. The mean values of the equilibrium constants were found by the method of least squares.

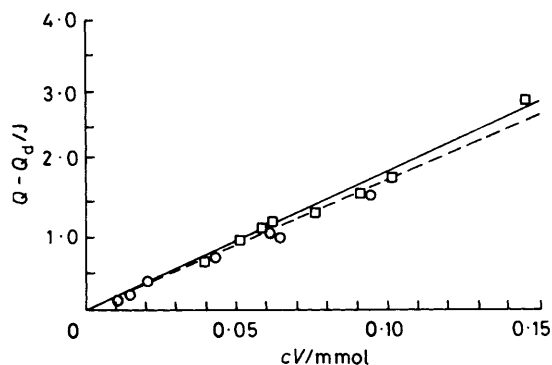


Figure 5. The plot $Q - Q_d$ versus n , where $n = cV$: \square hexane-1,6-diol; \circ octane-1,8-diol

Table. Thermodynamic parameters for reactions of triethylamine with hydroxy groups of diols

$K/\text{dm}^3 \text{ mol}^{-1}$	$-\Delta H^\circ/\text{kJ mol}^{-1}$	$-\Delta S^\circ/\text{J K}^{-1} \text{ mol}^{-1}$	$-\Delta G^\circ/\text{kJ mol}^{-1}$
Hexane-1,6-diol			
1.77 ± 0.06	18.4 ± 0.7	56.4	1.43
Octane-1,8-diol			
1.67 ± 0.04	17.4 ± 0.1	53.5	1.28

The determination of the equilibrium constants enabled the standard changes in enthalpy to be calculated. In order to do this, calorimetric measurements of the reaction of triethylamine with diols in dichloroethane were carried out. Standard changes in the enthalpy of complex formation were calculated according to the method of Arnett and his co-workers^{3,4} from equation (9) where Q is the measured effect, Q_d is the thermal effect of

$$\Delta H^\circ = (Q - Q_d)/c \cdot V \quad (9)$$

dissolution of triethylamine and is equal to $19.2 \pm 0.08 \text{ J g}^{-1}$, V is the volume of solution, c is the molar concentration of the complex in the equilibrium calculated from equation (10). The

$$2c = (c_{\text{OH}}^\circ + c_{\text{Et}_3\text{N}} + K^{-1}) - [(c_{\text{OH}}^\circ + c_{\text{Et}_3\text{N}} + K^{-1})^2 - 4c_{\text{OH}}^\circ \cdot c_{\text{Et}_3\text{N}}]^{1/2} \quad (10)$$

experimental data are shown in Figure 5 as a plot of $(Q - Q_d)$ against cV . The values of ΔH° for both compounds were found by the standard least squares technique as the directional coefficients of the observed straight lines. On the basis of the well known thermodynamic relationships (11) and (12)

$$\Delta G^\circ = -RT \ln K \quad (11)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (12)$$

standard changes in thermodynamic potentials and entropy were calculated. The values obtained are listed in the Table. Standard changes in the enthalpy of formation of complexes of triethylamine with the hydroxy groups of both diols were the same within experimental error which is in agreement with the results of the i.r. spectroscopic studies.

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