

STUDY OF THE PHASE EQUILIBRIUM
OF THE OLIGO(ETHYLENE OXIDE)–WATER SYSTEM
BY DIFFERENTIAL THERMAL ANALYSIS

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A DTA apparatus suitable for measuring polymer solutions has been constructed. With the use of this apparatus, the phase equilibrium was studied for various concentrations of the oligo(ethylene oxide)–water system. In the region of dilute solutions, the precipitation temperature was determined from the DTA curve, which exhibits a sigmoidal shape. Estimates were made of the thermodynamic parameters for entropy $\Psi_1 = -1.89$ and enthalpy $\kappa_1 = -1.86$ (at 380 K), and the theta temperature $\Theta = 101^\circ\text{C}$. In concentrated solutions the thermodynamic quantities characterizing the fusion of oligomers depend on the molecular weight, and the values estimated from DTA peak areas and from the equation for the melting point depression agree fairly well.

In dilute solutions of the oligo(ethylene oxide)–water system, the heats of dilution have been measured by using a twin micro-calorimeter, and the interaction enthalpy parameter, κ , has been estimated to be negative (exotherm) [1], while the entropy parameter, Ψ_1 , has been estimated to be negative by making use of a value of the second virial coefficient obtained by means of the osmotic pressure method [2]. The fact that both enthalpy and entropy parameters are negative in aqueous oligo(ethylene oxide) solutions may suggest the existence of a lower consolute temperature [3]. In order to confirm this phenomenon, a differential thermal analysis (DTA) method has been employed to study the phase equilibrium in dilute solutions of the oligo(ethylene oxide)–water system.

Further, the melting of oligo(ethylene oxide) samples has also been studied [4–6]. As reported by Malcolm and Rowlinson [7], the melting temperature of the oligomer decreases as the concentration decreases. This phenomenon seems to correspond to the dissolution of oligomer for concentrated oligomer solutions. In order to detect the dissolution of oligo(ethylene oxide) in the diluent, the DTA method has been applied to study the phase equilibrium in concentrated solutions.

Experimental

The DTA apparatus suitable for measuring polymer solutions was modified so as to seal the cell more perfectly than the one described in a previous paper [8]. The modified cell and cell holder are illustrated in Fig. 1. The cell holder is made of a copper block heated by a nichrome wire (25 Ω). The cell which has a capacity

of about 3 ml is made of glass. The portion *A* of the cell is sealed tightly with a small flame after the polymer solution has been poured into the cell, in order to prevent concentration change and evaporation of the solvent with increasing temperature. Although the thermal conductivity of glass is low, it is advantageous

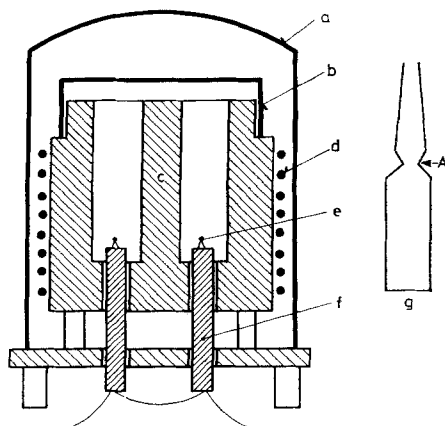


Fig. 1. DTA apparatus and cell. a: glass mantle; b: cover; c: cell holder: diameter 60 mm, height 50 mm; d: heater; e: thermocouples; f: thermocouple insulating tubes; g: glass cell: diameter 12 mm, height 30 mm

in that the cell is sealed easily and perfectly. The samples, with about 1.5 ml of oligomer solution for the dilute region and about 0.5 g of oligomer for the concentrated region, were measured, the reference materials being Al_2O_3 for the concentrated and water for the dilute solutions. The procedure with this apparatus is similar to that described previously [8]. The heating rate is about $0.62^\circ\text{C}/\text{min}$.

The molecular weights of the oligo(ethylene oxide) samples used in this study were $6 \cdot 10^3$ and $2 \cdot 10^4$, respectively. The water was purified by distillation.

Results and discussion

The phase equilibrium of dilute aqueous oligo(ethylene oxide) solutions

The phase equilibrium of the aqueous oligo(ethylene oxide) solutions was measured by using the DTA apparatus with the modified cell. The DTA curves obtained for aqueous oligomer solutions having concentrations of 10, 20 and 30 wt. % are shown in Fig. 2. Each curve is sigmoidal and goes into the exothermic direction at a definite temperature for the given oligomer solution. The precipitation temperature, T_p , was estimated from the DTA curve at the point *P* in the curve shown in Fig. 2, in a similar way as previously [8]. The plots of T_p against the concentration of oligomer are shown in Fig. 3.

A lower critical solution temperature can be seen to exist. The consolute temperature, T_c , and the critical composition, C_c , estimated are listed in Table 1, together with values estimated by another author [7]. T_c decreases with the molecular weight of the oligomer.

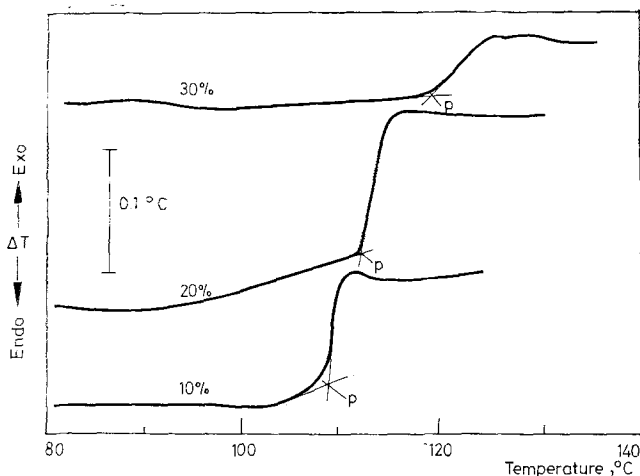


Fig. 2. DTA curves of oligo(ethylene oxide) ($M_w = 2 \cdot 10^4$)-water systems for various oligomer concentrations. P point: precipitation temperature

Table 1
Lower consolute temperature (T_c) and
critical composition (C_c) of aqueous oligo(ethylene oxide) solutions

$M_w \cdot 10^{-3}$	$T_c, ^\circ\text{C}$	$C_c, \text{wt}\%$
3*	157.5	25.1
5*	127.5	20.7
6	115	17.4
20	107	13.9

* See Ref. [7].

Following Flory's theory [9], T_c is expressed as a function of the molecular weight of the polymer as follows:

$$1/T_c = 1/\Theta \{1 + 1/\Psi_1 (1/X^{1/2} + 1/2X)\} \quad (1)$$

where Θ is the theta temperature of the polymer with infinite molecular weight, X is the degree of polymerization and Ψ_1 is the entropy parameter.

According to Eq. (1), plots of the reciprocal of T_c against the degree of polymerization function must be linear and the thermodynamic parameters, Ψ_1 , and

Θ , can be evaluated from the slope and intercept, respectively. The enthalpy parameter, κ_1 , equal to $\Psi_1 \Theta/T$, may be estimated from the values of Ψ_1 and Θ . The results obtained for the oligomer-water systems are not sufficient to yield a straight line as was found for lower molecular weight oligo(ethylene oxide),

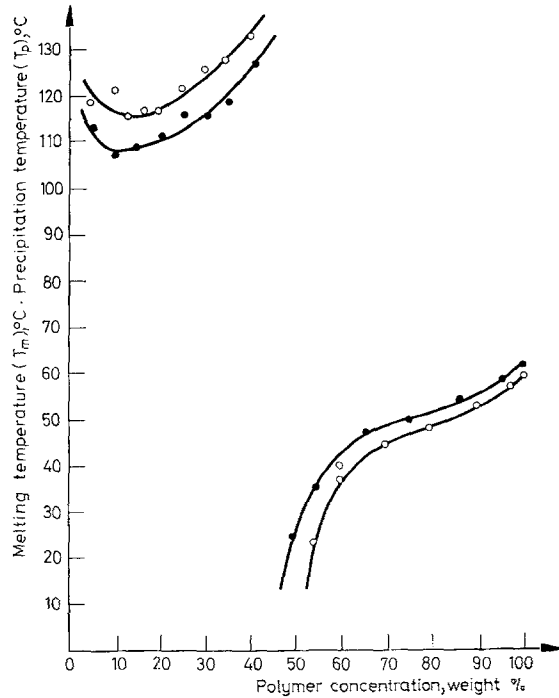


Fig. 3. Plots of precipitation temperature and melting temperature against concentration of oligo(ethylene oxide) for molecular weights —●— $6 \cdot 10^3$ and —○— $2 \cdot 10^4$

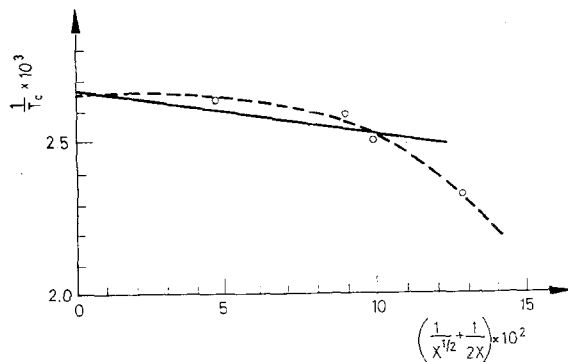


Fig. 4. Plots of $1/T_c$ against degree of polymerization function

shown by the dotted line in Fig. 4. However, the tentative plots give a straight line with considerable error, as shown by the solid black line in Fig. 4. The thermodynamic parameters estimated from these rough plots are listed in Table 2, together with those obtained previously [12]. It can be seen from Table 2 that the thermodynamic parameters obtained by the DTA method are correct in sign, but not in absolute values. This discrepancy may be due to two factors. The first is that the thermodynamic parameters estimated with Flory's equation (Eq. (1)) correspond to the values at infinite molecular weight, whereas those estimated in this study involve an error of extrapolation from a molecular weight of less than $2 \cdot 10^4$ to infinity. The other factor may be the dependence of the thermodynamic parameters on temperature. For the elucidation of this problem further study is needed.

Table 2

Thermodynamic parameters of aqueous oligo(ethylene oxide) solution

	This study	Literature data
Θ	101°C	
Ψ_1	-1.89	-0.21 [2]
$\kappa_1 (= \Psi_1\Theta/T)$	-1.86 (at 107°C)	-0.27 [1] (at 25°C)

The phase equilibrium of concentrated solutions of oligo(ethylene oxide)

The phase equilibrium of concentrated aqueous solutions of oligo(ethylene oxide) was studied using the same DTA apparatus. The oligo(ethylene oxide) samples with molecular weights of $6 \cdot 10^3$ and $2 \cdot 10^4$ used in this study do not dissolve perfectly in water at room temperature in the region above 50 wt.% of oligomer.

As shown in Fig. 5, the DTA curve of pure oligo(ethylene oxide) with a molecular weight of $2 \cdot 10^4$ exhibits one endothermic peak at 62.8°, which corresponds to the fusion. In contrast, the sample with a molecular weight of $6 \cdot 10^3$ leads to two peaks at about 58.2 and 62.8°. These latter may correspond to two crystalline forms with extended- and folded-chain crystals, and the one peak in the former curve to the folded-chain crystal, as reported by Beech et al. [6].

The DTA curves obtained for the oligo(ethylene oxide) ($M_w = 2 \cdot 10^4$)-water system with various proportions of oligomer are also shown in Fig. 5. As the amount of diluent increases, the dissolution peak gradually becomes broader and the peak temperature decreases. For the oligomer with a molecular weight of $6 \cdot 10^3$, the DTA curves exhibit a broad peak similar to that obtained for the sample with molecular weight of $2 \cdot 10^4$, but different from that obtained for pure oligo(ethylene oxide).

Plots of dissolution temperature against concentration of oligomer for the oligo(ethylene oxide)-water system are shown in Fig. 3. The dissolution temperature decreases gradually with increasing solvent content down to about 70 wt. % of the oligomer, but in the oligomer concentration range of 70 to 50 wt. % the dissolution temperature decreases rapidly with the diluent content.

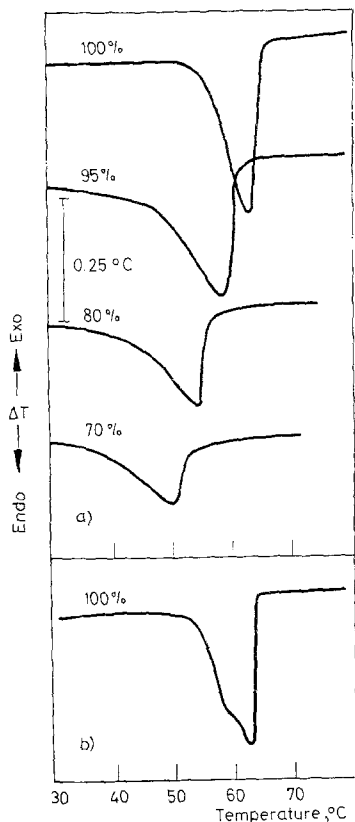


Fig. 5. (a) DTA curves of oligo(ethylene oxide)-water systems for various concentrations of oligomer with a molecular weight of $2 \cdot 10^4$; (b) DTA curve of pure sample with a molecular weight of $6 \cdot 10^3$

The effect of the diluent for the concentrated polymer-diluent mixture is represented by the following equation for the melting point depression:

$$1/T_m - 1/T_m^0 = (R/\Delta H_u) (V_u/v_1) (u_1 - \kappa_1 u_1) \quad (2)$$

where T_m^0 and T_m are the melting temperatures of pure polymer and polymer with diluent, respectively; ΔH_u is the heat of fusion of the polymer per unit molecular structure; V_u is the unit molar volume of the polymer; v_1 is the molar volume of the diluent; u_1 is the volume fraction of the diluent; κ_1 is the interaction

Table 3

Melting temperatures (T_m^0) and heats of fusion (ΔH_u) of oligo(ethylene oxide)

Mol. wt.	T_m^0 , °C	ΔH_u , kcal/unit mol	Method	Reference
$6 \cdot 10^3$	58.2 or 61.3	2.07	DTA	this study
	61.0	2.09	Flory equation	this study
	61.0 or 64.1	—	dilatometer	Beech et al. [6]
$2 \cdot 10^4$	62.0	1.94	DTA	this study
	64.5	1.97	Flory equation	this study
	65.8 or 66.4	—	dilatometer	Beech et al. [6]
	62.8	1.96	specific heat	Beaumont et al. [4]

parameter. The melting point of the pure oligomer (T_m^0) is estimated from the intercept of the plots of $1/T_m$ against u_1 . The melting point of pure oligo(ethylene oxide) with molecular weights of $6 \cdot 10^3$ and $2 \cdot 10^4$ are about 61.0 and 64.5°, respectively, which are comparable to those estimated from the peak temperatures of the DTA curve and those reported by other authors [4, 6] as shown in Table 3.

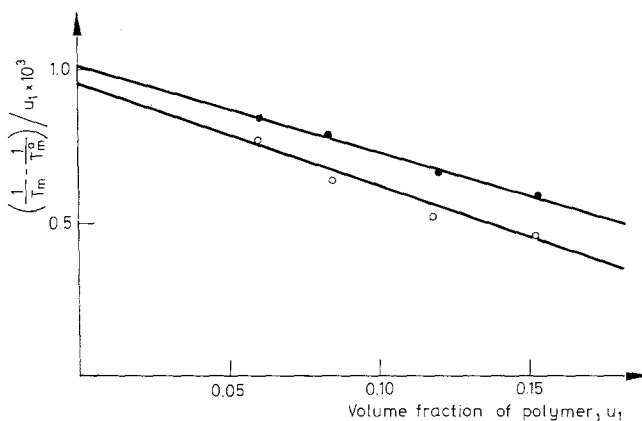


Fig. 6. Plots of $(1/T_m - 1/T_m^0)/u_1$ against volume fraction of solvent (u_1) for molecular weights of oligo(ethylene oxide) —●— $2 \cdot 10^4$ and —○— $6 \cdot 10^3$

By taking the melting temperatures of the pure oligomers as 61.0 and 64.5°, respectively, plots of $(1/T_m - 1/T_m^0)/u_1$ against u_1 (see Eq. (2)) give straight lines (Fig. 6), and ΔH_u and x_1 are estimated from the intercept and slope, respectively.

The estimated heats of fusion of the oligomers are listed in Table 3, together

with those estimated from the peak area of the DTA curves and those determined by other authors [4, 6]. The values obtained in this study are in good agreement with those reported by other authors. The heat of fusion for the oligomer with a molecular weight of $2 \cdot 10^4$ is less than that for the one with a molecular weight of $6 \cdot 10^3$.

In concentrated solutions of the oligomers, the interaction parameters κ_1 are about -3.43 and -2.89 for molecular weights of $6 \cdot 10^3$ and $2 \cdot 10^4$, respectively, and are considerably larger than those estimated from the diluent solutions. This discrepancy may be ascribed to the dependence of the interaction parameter on the concentration of polymer.

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RÉSUMÉ — On a construit un appareil ATD pour l'étude des polymères en solution. A l'aide de cet appareil, on a étudié les équilibres de phases dans tout le domaine de concentrations du système oligo(oxyde d'éthylène)-eau. Pour les solutions diluées, on a déterminé la température de précipitation à partir de la courbe ATD de forme sigmoïde. On a estimé les paramètres thermodynamiques de l'entropie ($\Psi_1 = -1.89$) et de l'enthalpie ($\kappa_1 = -1.86$) à 380 K, ainsi que la température θ : $\theta = 101^\circ\text{C}$.

Pour les solutions concentrées, les quantités thermodynamiques caractéristiques de la fusion de l'oligomère dépendent du poids moléculaire et les valeurs obtenues en se servant de la température au sommet du pic ATD sont en bon accord avec celles de l'équation donnant l'abaissement du point de fusion.

ZUSAMMENFASSUNG — Ein zur Messung von Polymerlösungen geeignetes DTA-Gerät wurde konstruiert. Mit Hilfe dieses Gerätes wurden die Phasengleichgewichte sämtlicher Konzentrationen des Systems Oligo(äthylenoxid)-Wasser studiert. Im Bereich der verdünnten Lösung wurde die Präzipitierungstemperatur aus der sigmoiden DTA-Kurve bestimmt. Die thermo-

dynamischen Parameter der Entropie $\Psi_1 = -1.89$ und der Enthalpie $\kappa_1 = -1.86$ (bei 380 K) sowie die Theta-Temperatur $\Theta = 101^\circ\text{C}$ wurden ermittelt.

Während in konzentrierten Lösungen die thermodynamischen Größen, welche für das Schmelzen des Oligomers bezeichnend sind, vom Molekulargewicht abhängen, sind die aus dem Peak der DTA-Kurve und der Gleichung für die Herabsetzung des Schmelzpunktes ermittelten Werte in guter Übereinstimmung.

Резюме — Описана конструкция прибора ДТА, пригодного для измерения полимерных растворов. С помощью этого прибора изучено фазовое равновесие по всей концентрации системы олигоэтиленоксид — вода. По кривой ДТА сигмоидальной формы, определена температура осаждения в области разбавленного раствора. Расчитаны термодинамические параметры энтропии $\Psi = 1,89$ и энтальпии $\kappa_1 = -1,86$ (при 380 K) и температура $\Theta = 101^\circ\text{C}$. В случае концентрированного раствора термодинамические величины, характеризующие плавление олигомеров, зависят от молекулярного веса и их значение можно довольно хорошо определить по пику кривой ДТА и уравнению для депрессии точек плавления.