Mixing of ethylene oxide and propylene oxide oligomers: 2. Phase separation

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(Received 31 August 1976)

Equilibrium phase compositions and cloud point curves have been determined for mixtures of ethylene oxide and propylene oxide oligomers. Large differences in miscibility are noted between α,ω-hydroxy- and α,ω-methoxy-oligomers. The data for the α,ω-methoxy-oligomers are simply interpreted in terms of the Flory–Huggins equation with concentration dependent χ, i.e. $\chi = \chi_0 + \chi_1\phi_1$ where ϕ_1 is the volume fraction of component 1. The approximate value of χ for the α,ω-methoxy-oligomer mixtures is found to be 0.1.

INTRODUCTION

In part 1[1] we have reported enthalpy and volume changes on mixing ethylene oxide and propylene oxide oligomers. The free energy of mixing is less accessible experimentally. One method of investigation is the determination of equilibrium phase compositions in partly miscible mixtures. The interpretation of such data is complicated by the extreme sensitivity of the binodial to the form of the free energy of mixing function[2,3]. The results of part 1[1] point to a complex free energy function. Koningsveld *et al.*[2] have discussed this problem and suggested the formal approach to the analysis of phase behaviour, in terms of a generalized Flory–Huggins model, which we will adopt here. In this work we avoid some of the complications of interpretation by working with samples of narrow molecular weight distribution so that fractionation effects during phase separation are unimportant.

EXPERIMENTAL

Materials

The α,ω-hydroxy-oligomers used in this work were obtained from commercial sources: samples E300H, P1000H and P1500H from Shell Chemical Co. Ltd, sample E600H from Hoechst Chemicals Ltd, and sample P2025H from Koch-Light and Co. Ltd. (The prefix, E or P, denotes an ethylene oxide or a propylene oxide oligomer; the number denotes the molecular weight quoted by the manufacturer; the suffix H denotes hydroxy-end-groups.) The molecular weights were checked by gel permeation chromatography (g.p.c.—see later for details): a comparison with standard samples showed that the quoted values of $\bar{M}_n$ were sufficiently accurate for our purposes. All samples had narrow molecular weight distributions: the ratios $\bar{M}_w/\bar{M}_n$ found by g.p.c. were less than 1.05. Before use all samples were dried for 2 weeks or more under high vacuum (<1 Pa) to reduce the water content to less than 0.1 wt %.

The α,ω-hydroxy-oligomers were methoxylated by the modified Williamson ether synthesis described earlier[1]. Infra-red spectroscopy, elemental analysis and end-group analysis (phthaloylation in pyridine[4]) were used to confirm a conversion of hydroxy- to methoxy- groups of about 99.7%. The molecular weight distributions, as determined by g.p.c., were unchanged in shape by the methoxylation process. The α,ω-methoxy-oligomers are denoted by suffix M.

Specific volumes

Specific volumes of the oligomers at 30° and 40°C were measured by means of small (1 to 2 cm^3) picnometers to an accuracy of ±0.002 cm^3/g.

Equilibrium phase compositions

Phase equilibration was carried out in graduated pyrex tubes of ~5 cm^3 capacity and 15 cm length. The tubes were calibrated (cm^3/cm) by means of distilled water from a burette. Usually six tubes were used for experiments with a given polymer pair. In an experiment the tubes were dried thoroughly before weighing in the two oligomers in the required proportions (i.e. overall volume fraction of a component ranging from 0.25 to 0.75). The tubes were stoppered, making use of silicone grease to ensure a seal impervious to water vapour. The tubes were repeatedly inverted, in order to disperse the two oligomers, and then equilibrated in a water bath held at 30° ± 0.01°C. When the phases became clear the phase volumes were noted. The dispersion and equilibration procedures were repeated until constant phase volumes were obtained. Samples of the two phases were then extracted with syringes. Phase compositions were estimated in 3 different ways.

Phase Volume (PhV). Assuming a binary mixture and ignoring small volume changes on mixing[1] the total volumes, V_1 and V_2, of the two components in the system are given by:

$$V_1 = V'\phi_1' + V''\phi_1'' \tag{1}$$

$$V_2 = V'(1 - \phi_1') + V''(1 - \phi_1'') \tag{2}$$

where V and ϕ_1 represent, respectively, the phase volume and the volume fraction of component 1 in the phase, and the two phases are denoted prime and double prime. From 6 tubes we generate a total of 12 equations from which to evaluate the two variables ϕ_1' and ϕ_1''. Accordingly we used a least squares method for this calculation.

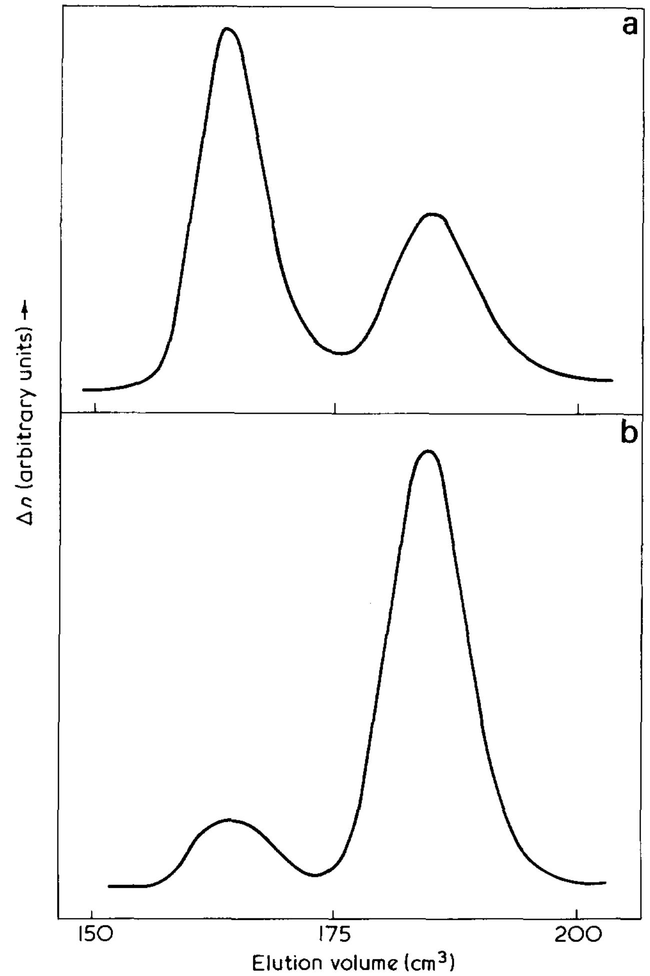

Figure 1 Chromatograms of mixtures of E600M and P2025M: (a) upper phase and (b) lower phase

Refractometry (RI). Refractive indices were determined at 40° ± 0.1°C by means of an Abbé refractometer. Calibration was with pure components and with homogeneous mixtures of known composition. A linear variation of refractive index with ϕ_1 was found in every case: this is in keeping with the Gladstone–Dale relationship[5].

Gel permeation chromatography (g.p.c.). Conditions for g.p.c. were as follows: 5 x 4 ft columns packed with Styragel with nominal pore sizes in the range 15 to 1500 nm; tetrahydrofuran at 25°C and flow rate 1 cm^3/min; injection of 65 mm^3 of solution of concentration ~0.04 g/cm^3. Under these conditions all the oligomer pairs except E600H/P1000H were sufficiently well resolved to allow the areas under the peaks (detected by an Optilab Multiref 901 refractometer) to be assessed (see, for example, *Figure 1*). Calibration with pure components and mixtures of known compositions yielded a linear variation of relative peak area with ϕ_1 in every case.

Cloud points

Clouding and clearing temperature were determined for polymer mixtures sealed into small tubes (~0.5 cm^3 capacity, ~5 cm length). Usually 9 tubes were used to cover the composition range $\phi_1 = 0.1$ to 0.9. The tubes were dried thoroughly before weighing in the polymers. They were then evacuated and sealed with a flame. The sealed tubes were shaken in a water bath at 25° ± 0.01°C; 6 h were allowed for equilibration. Clearing temperatures were obtained by increasing the temperature by 0.2K each day. Clouding temperatures were obtained by lowering the temperature by 0.2K/day.

RESULTS

The specific volumes are listed in *Table 1*. They are consistent with published values of specific volumes and temperature coefficients of specific volumes for ethylene oxide[6] and propylene oxide[6,7] oligomers. They are used in this work to calculate volume fractions. They also serve to show that the volume fractions are practically independent of temperature over the small temperature range of our experiments.

Preliminary investigation of the miscibility of ethylene oxide and propylene oxide oligomers showed that mixtures of E300H or E600H with P1000H, P1500H or P2025H were partly miscible at or about 30°C. Mixtures of E300H or E600H with P750H were completely miscible at 30°C. The α,ω-methoxy-oligomers were more miscible, only E600M with P2025M being partly miscible at 30°C. Ethylene oxide oligomers of higher molecular weight (e.g. E1000H or E1000M) crystallized at 30°C from mixtures with propylene oxide oligomers (e.g. P425H or P425M).

Phase compositions are listed in *Table 2*. The lower phase is denoted prime, the upper phase double prime. Component 1 is the ethylene oxide oligomer. The precision of ϕ'_1 or ϕ''_1 is estimated to be about ±0.02 (*PhV*), ±0.03 (*RI*) and ±0.05 (g.p.c.). The best estimates of ϕ'_1 and ϕ''_1 are weighted averages of the results obtained by the three techniques.

Cloud points are plotted in *Figure 2*. The equilibrium phase compositions found for the system E600M/P2025M at 30°C are plotted in *Figure 2* and are seen to be consistent with the cloud points. This is evidence that the mixture of E600M with P2025M behaves as a binary system.

The g.p.c. method permits the molecular weight distributions of the oligomers to be determined *after phase separation*. No differences in molecular weight distribution could be detected with any mixture involving E600H or E600M. In mixtures involving E300H small differences in its molecular weight distribution could be detected. These were towards preferential solubility of the shortest chains in the upper phase, i.e. the phase most dilute in E300H. The differences were small, corresponding to $\bar{M}'_n - \bar{M}''_n \leqslant 10$. We conclude that the mixtures involving E300M exhibit molecular fractionation and so cannot be treated as binary systems.

Table 1 Specific volumes (cm^3/g) of ethylene oxide and propylene oxide oligomers

Sample	T = 30°C	T = 40°C
E300H	0.896	0.901
E600H	0.893	0.901
E300M	0.963	0.971
E600M	0.933	0.942
P1000H	1.003	1.012
P1500H	1.004	1.011
P2025H	1.007	1.014
P1000M	1.023	1.030
P1500M	1.015	1.021
P2025M	1.012	1.018

Table 2 Equilibrium phase compositions for mixtures of ethylene oxide and propylene oxide oligomers at 30°C

	ϕ_1' (lower phase)*				ϕ_1'' (upper phase)*			
Mixture	*PhV*	*RI*	G.p.c.	Best	*PhV*	*RI*	G.p.c.	Best
E300H/P1000H	0.67	0.79	0.76	0.74	0.34	0.35	0.28	0.33
E300H/P1500H	0.98	0.98	0.97	0.98	0.10	0.14	0.10	0.11
E300H/P2025H	0.99	0.98	0.98	0.98	0.07	0.06	0.08	0.07
E600H/P1000H	0.81	0.80	–	0.80	0.18	0.20	–	0.19
E600H/P1500H	0.97	0.98	0.97	0.97	0.05	0.08	0.08	0.07
E600H/P2025H	0.97	0.98	0.98	0.98	0.06	0.01	0.01	0.03
E600M/P2025M	0.79	0.77	0.78	0.78	0.36	0.34	0.33	0.34

*Volume fraction of poly(ethylene oxide)

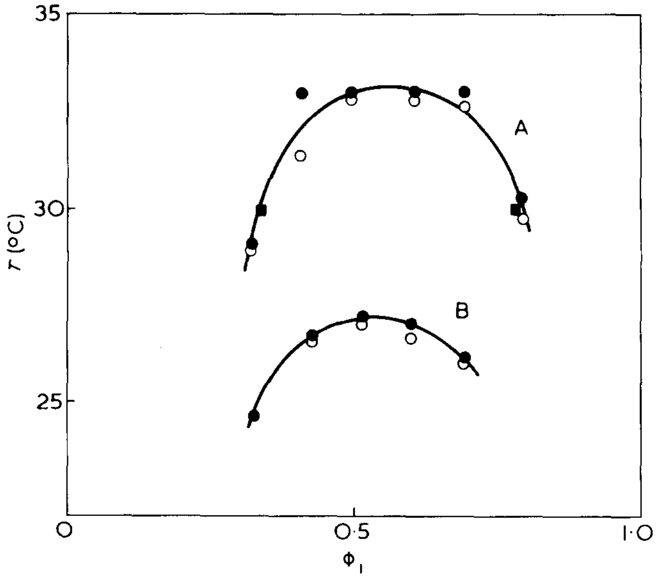

Figure 2 Cloud point curves: A, E600M/P2025M and B, E600M/P1500M. Clouding temperatures (○), clearing temperatures (●) and equilibrium phase compositions (■) are depicted

DISCUSSION

The differences in miscibility between oligomers noted in this work (and quantified in *Table 2*) demonstrates the importance of the end-group interactions in the thermodynamics of mixing. We have remarked upon this earlier^1.

In part 1^1 we recognized end effects in the enthalpies of mixing of α,ω-hydroxy-oligomers (and the possibility of such effects in the mixing of α,ω-methoxy-oligomers) as well as, via the volume change on mixing, the existence of effects due to the differing nature of the oligomeric liquids. A proper explanation of our results would require account to be taken of all these contributions. We do not have sufficiently good initial data for such an analysis.

If we ignore equation of state effects and restrict our immediate discussion to α,ω-methoxy-oligomers we have only to account for the finding^1 that the enthalpy of mixing function $\Delta H_m/R\phi_1\phi_2$ is a linear function of ϕ_1. [This is the concentration dependence predicted for a system in which the total interchange energy depends upon the product of site (surface) fractions, $\theta_1\theta_2$, and in which other effects are unimportant.] Koningsveld *et al.*^{2} have suggested that such a model system is best discussed in terms of the Flory–Huggins equation with a concentration dependent χ parameter. Accordingly we write, assuming a binary system, the free energy of mixing per mole of segments (ΔG_m) as:

$$\frac{\Delta G_m}{RT} = \frac{\phi_1}{r_1}\ln\phi_1 + \frac{\phi_2}{r_2}\ln\phi_2 + \chi\phi_1\phi_2 \tag{3}$$

where

$$\chi = \chi_0 + \chi_1\phi_1 \tag{4}$$

The segment size is arbitrary. We find it convenient to define the segment size as the volume of a poly(ethylene oxide) midchain unit. Thus the chain length of the oligomers in segments, r_1 and r_2, can be written:

$$r_1 = M_1/44 \tag{5}$$

$$r_2 = M_2 v_{2,sp}/M_1 v_{1,sp} \tag{6}$$

Taking each term in χ to be linearly dependent on $1/T$ leads to^2:

$$\chi_0 = \chi_{0,1} + \chi_{0,2}/T \tag{7}$$

$$\chi_1 = \chi_{1,1} + \chi_{1,2}/T \tag{8}$$

and so to an expression for the enthalpy of mixing per mole of segments (ΔH_m)

$$\frac{\Delta H_m}{R} = \phi_1\phi_2(\chi_{0,2} + \chi_{1,2}\phi_1) \tag{9}$$

which is of the form found experimentally^1.

We have calculated binodials for the system E600M/P2025M taking $M_1 = 628, M_2 = 2053$. They are plotted in *Figure 3*, the values of χ_1 being chosen so that the critical values* of ϕ_1 are in the range 0.5 to 0.7. Comparison of the experimental cloud point curve for the system E600M/P2025M (*Figure 2*, $\phi_{1,c} \simeq 0.56$, $T_c \simeq 306.3$K) with the

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* Given that $\chi = \chi_0 + \chi_1\phi_1$ the critical conditions:

$$\frac{\partial^2 \Delta G_m}{\partial \phi_1^2} = \frac{\partial^3 \Delta G_m}{\partial \phi_1^3} = 0$$

lead to

$$\frac{1}{r_1\phi_{1c}} + \frac{1}{r_2\phi_{2c}} - 2\chi_0 + 2\chi_1(1 - 3\phi_1) = 0$$

and

$$-\frac{1}{r_1\phi_{1c}^2} + \frac{1}{r_2\phi_{2c}^2} - 6\chi_1 = 0$$

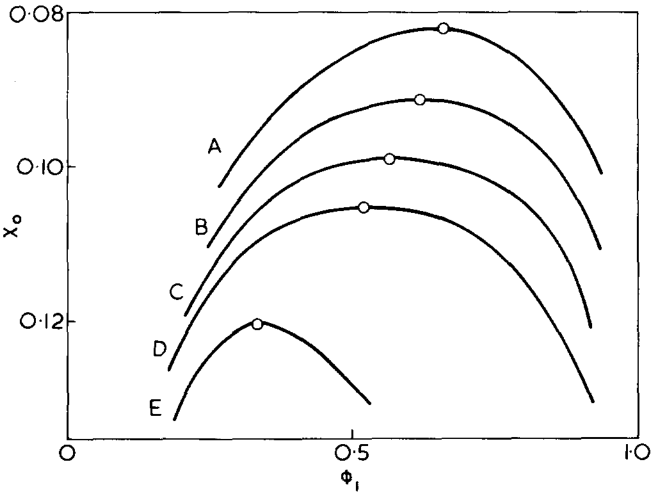

Figure 3 Binodials for the system E600M/P2025M calculated according to equations (3) and (4) assuming a value of χ_1: A, 0.0; B, –0.01; C, –0.02; D, –0.03; E, –0.10. ○, Represent critical points

Table 3 Approximate values of the free energy parameter χ at 30°C

Mixture	Cloud point curve	Equilibrium phase concentrations
E600M/P1500M	(0.106–0.086)*	–
E600M/P2025M	0.104–0.084	0.091
E600H/P1000H	–	0.13
E600H/P1500H	–	0.16
E600H/P2025H	–	0.17

*At T = 27°C

calculated curves allows one to choose that calculated with $\chi_1 = -0.02$ (*Figure 3*, $\phi_{1,c} = 0.56$, $\chi_{0,c} = 0.099$) as the most appropriate. A similar comparison of calculated and experimental curves for the system E600M/P1500M leads to the same value of $\chi_1 = -0.02$. This value of χ_1 is consistent in sign and in approximate magnitude with that predicted for $\chi_{1,2}/T$ from the enthalpies of mixing of miscible ethylene oxide and propylene oxide oligomers (see Table 4 of Ref 1)

We do not believe our data to be of sufficient precision to merit a more detailed analysis in terms of equations (3) to (9).

An approximate value of the overall parameter χ is useful for the prediction of equilibrium effects which are less sensitive to the exact value of χ than is the miscibility. The cloud point curves, analysed as above, give one such estimate (*Table 3*). A second estimate can be obtained from the equilibrium phase concentrations by applying the equilibrium conditions:

$$\mu_1' = \mu_1'', \mu_2' = \mu_2'' \tag{10}$$

to obtain the equation (for constant χ)

$$\chi = \frac{\ln \left[\left(\frac{\phi_1'}{\phi_1''} \right)^{r_2} \left(\frac{\phi_2''}{\phi_2'} \right)^{r_1} \right]}{2r_1 r_2 (\phi_1' - \phi_1'')} \tag{11}$$

The values of χ calculated using equation (11) for system E600M/P2025M is consistent with that obtained from the more searching analysis of the cloud point curve (see *Table 3*). Values of χ calculated for the mixtures of α,ω-hydroxy-oligomers involving E600H are also given in *Table 3*. No values of χ are calculated for the mixtures involving E300H since fractionation was detected in these systems. Similar values (per ethylene oxide chain unit) have been reported recently[8] for mixtures of E15000H and P1050H.

The approximate value of χ found for the mixtures of α,ω-methoxy-oligomers, i.e. $\chi = 0.1$, has been used in a discussion of the thermodynamics of crystallization of ethylene oxide/propylene oxide block copolymers[9].

ACKNOWLEDGEMENTS

We thank Messrs D. J. Roy and D. Rowlinson for assistance with the characterization of the oligomers and with the g.p.c. analyses. We thank Dr Y. K. Leung for helpful discussions. A. F. acknowledges receipt of a Science Research Council Advanced Course Studentship.

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