Molecular Weight Dependence of the Heats of Hydration of Some Oligomeric Ethylene Oxides and Their Methoxyl Derivatives

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SYNOPSIS

The molecular weight dependence of the heat of hydration of the oligomeric ethylene oxides and their monomethoxyl and dimethoxyl derivatives has been studied using microcalorimetry. In all cases the molar heat of hydration decreased rapidly at low molecular weights reaching an asymptote at molecular weights in excess of 400. Equivalent values were obtained between oligomers and blends of the same average molecular weight. The data followed the Flory relationship relating the property of a polymer to the reciprocal of its molecular weight. However, the gradient for the oligomeric ethylene oxides was different from that of the two methoxyl derivatives suggesting a change in chain configuration. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

It is well known that when the oligomeric ethylene oxides are mixed with water, heat is evolved in an exothermic reaction primarily as a result of hydration of the ether linkage by hydrogen bond formation.[1-3] In fact Lakhanpal et al.[1] suggested that in excess water the bonds are formed quantitatively. A similar exothermic reaction has also been seen for nonionic surfactants where the hydrophilic group is a derivative of ethylene oxide.[4,5] Recent experiments with the nonylphenol ethoxylates (a series of nonionic surfactants with increasing chain length of ethylene oxide) has shown an increase in the heat of hydration with an increasing number of ethylene oxide units with a maximum chain length of 10 units, thereafter falling with increasing chain length of 30 units.[5] In this work the molecular weight dependence of the heat of hydration of the oligomeric ethylene oxides and their methoxyl derivatives has been studied using microcalorimetry.

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EXPERIMENTAL

All materials were used as received from Aldrich Chemical Co. Ltd., U.K. The materials studied were ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, pentaethylene glycol, hexa-

Table I   Molecular Weight Distribution of PEG200 and PEG300[8]

Glycol	PEG200 (%)	PEG300 (%)
Ethylene glycol	0.1	—
Diethylene glycol	3.4	0.4
Triethylene glycol	21.2	2.4
Tetraethylene glycol	31.2	9.0
Pentaethylene glycol	24.4	16.1
Hexaethylene glycol	14.0	25.5
Heptaethylene glycol	5.4	25.3
Octaethylene glycol	0.3	15.0
Nonaethylene glycol	—	4.2
Decaethylene glycol	—	2.0

ethylene glycol, heptaethylene glycol, and the polyethylene glycols of molecular weight 200, 300, 400, and 600. In addition the methoxyl derivatives, the monomethyl ethers of ethylene, diethylene, triethylene glycols, polyethylene glycol 350, and polyethylene glycol 550 were studied. For completeness the dimethyl ethers of ethylene, diethylene, triethylene, and tetraethylene glycols were also tested.

The heats of hydration of liquid samples in excess water at 25 ± 0.01°C were measured using a microcalorimeter (Model 458, Tronac Inc., Utah, USA). This calorimeter consisted of a reaction vessel (50-mL capacity silvered glass, vacuum, Dewar flask) immersed in a thermostatted, insulated water bath. The glycol (0.7–1.0 g) in its liquid state was contained in a sealed thin walled, glass ampoule
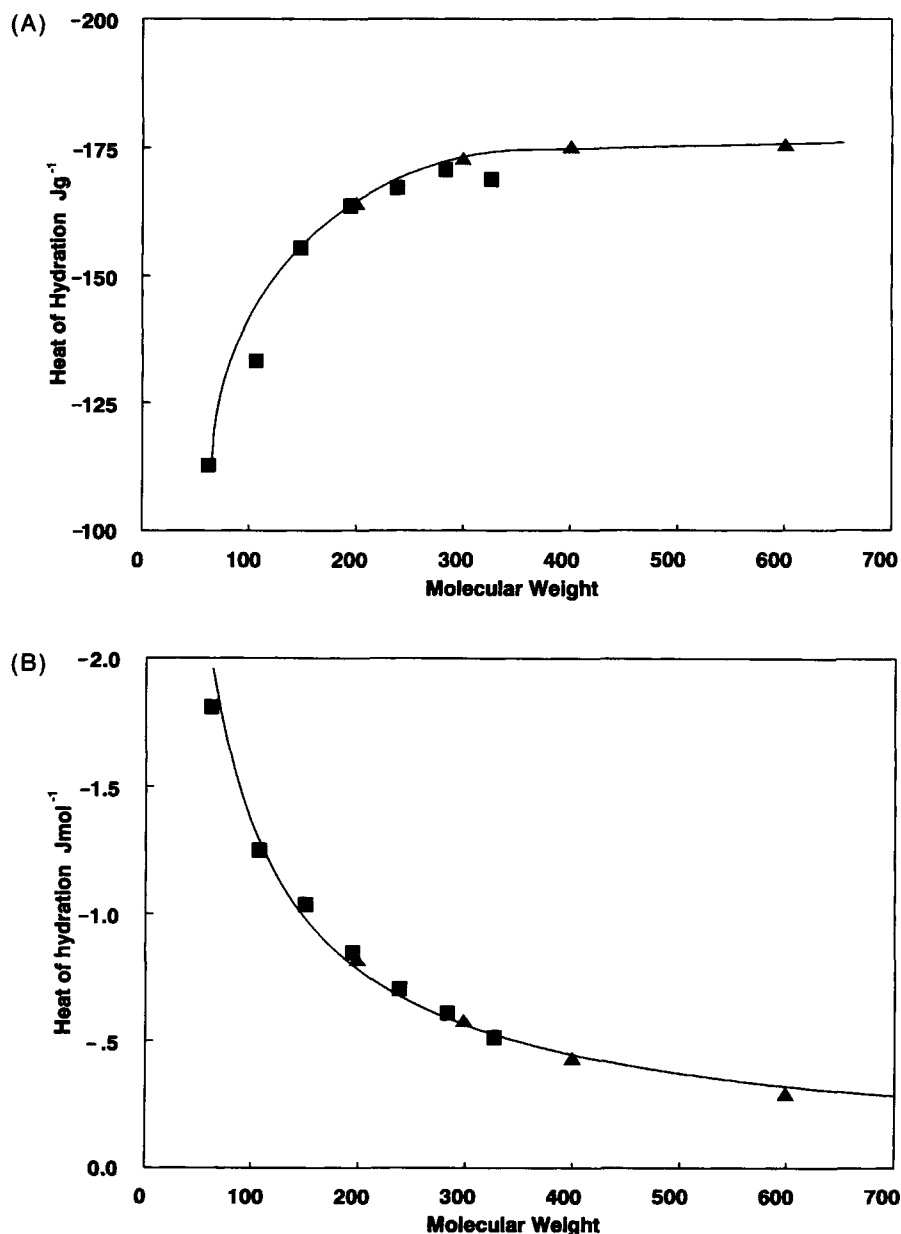

Figure 1 The effect of the molecular weight of the oligomeric ethylene oxides on the measured heat of hydration both on (A) weight and (B) molar basis. (■) Single oligomeric species. (▲) Commercial blends.

Table II   Comparison of Observed and Predicted Heats of Hydration

Mixture/Blend	Heat of Hydration J g^{-1}	
	Observed	Predicted
25/75[a]	−155.6	−156.0
50/50[a]	−147.7	−148.2
75/25[a]	−140.8	−140.4
PEG200	−164.0	−162.9
PEG300	−172.9	−169.7

[a] w/w ratio for diethylene glycol and tetraethylene glycol.

mounted on a rotating support that also doubled as a stirrer for the water in the reaction vessel. After equilibration to the required temperature, the ampoule was broken and the temperature rise monitored by means of a thermistor. This was compared to a similar temperature rise initiated by a heating coil in the reaction vessel and from the applied current, voltage, and time an enthalpy of reaction could be calculated. Data capturing and processing was carried out using a microcomputer linked to the calorimeter via an interface. All experiments were car-
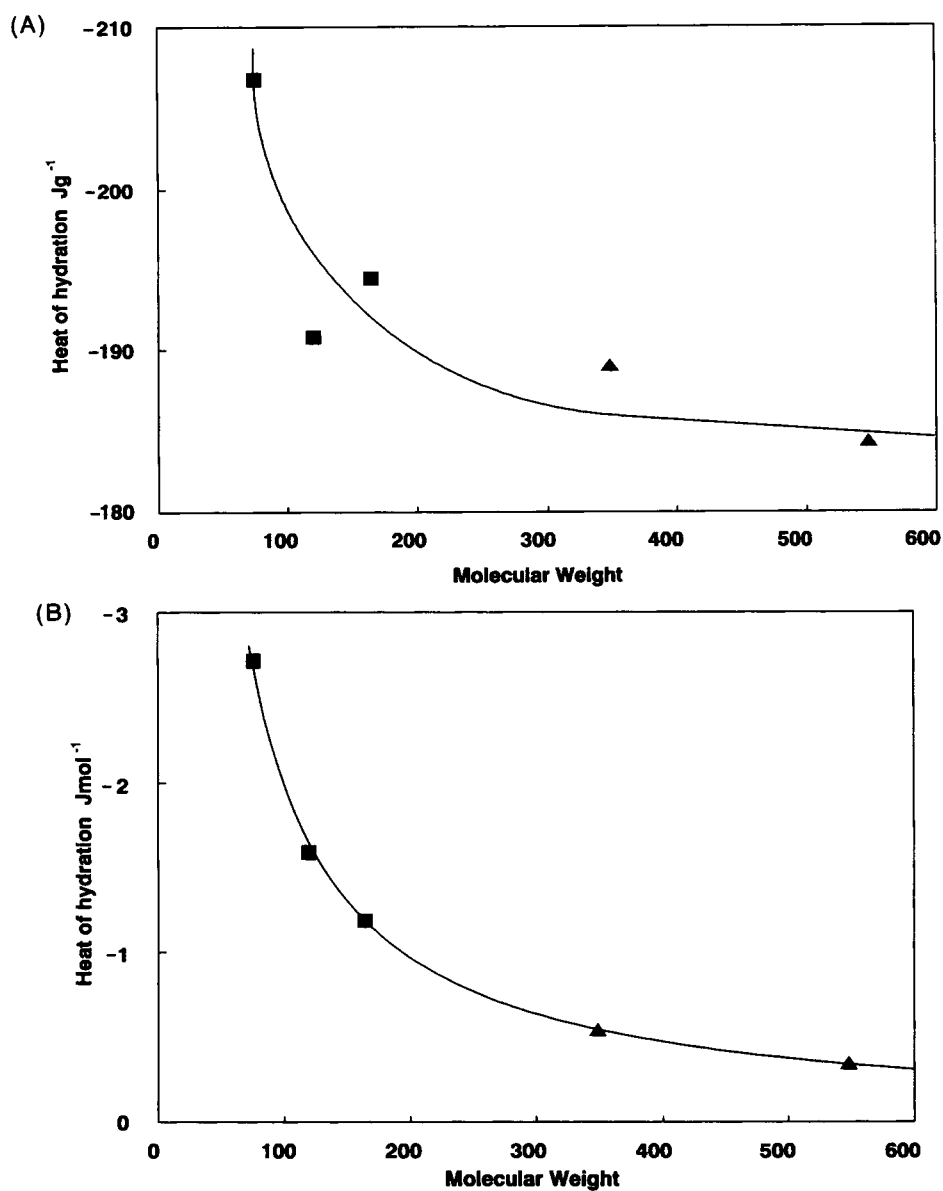

Figure 2   The effect of the molecular weight of the monomethoxyl derivatives of the polyethylene oxides on the measured heat of hydration both on (A) weight and (B) molar basis. (■) Single oligomeric species. (▲) Commercial blends.
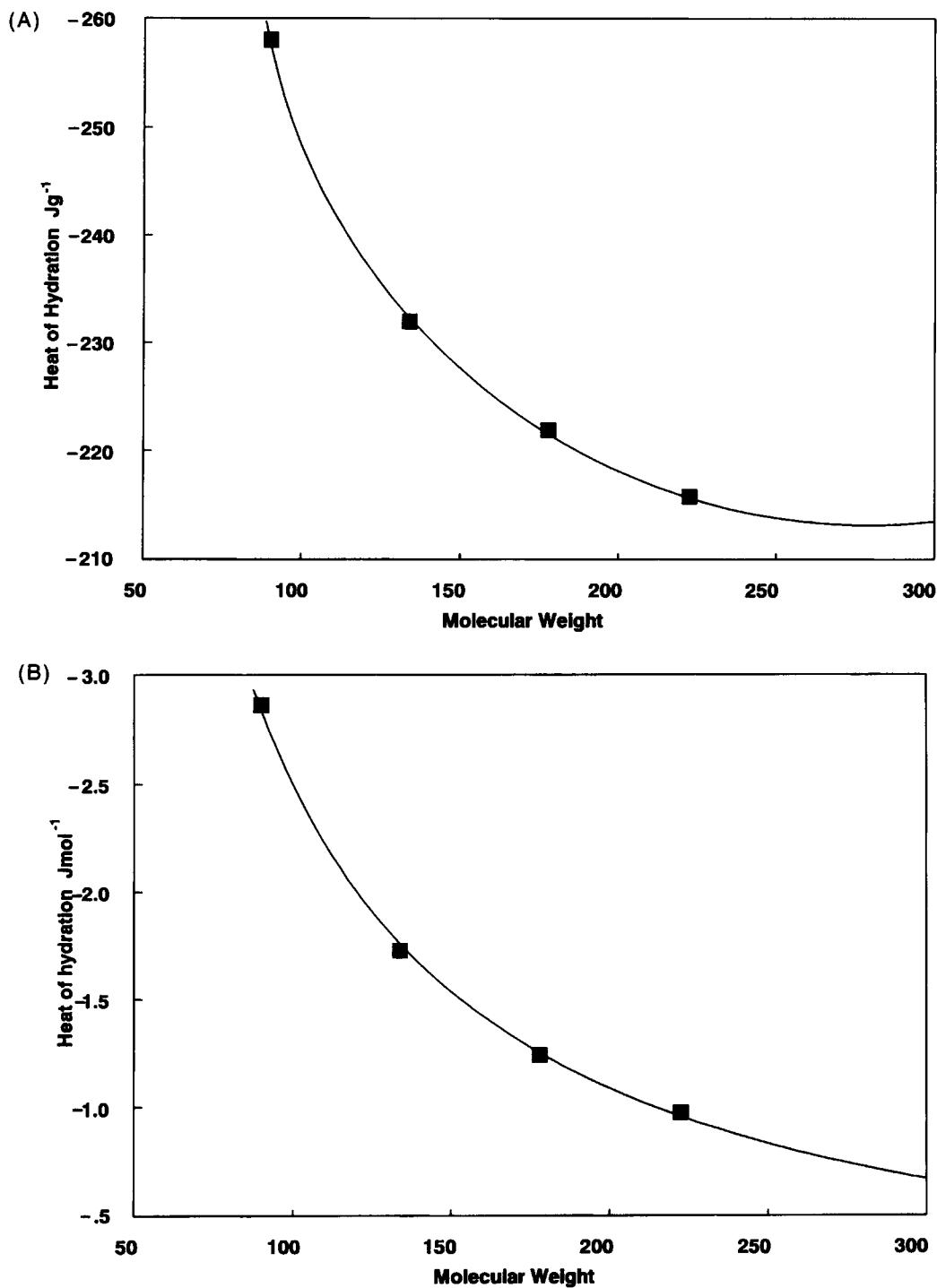
Figure 3   The effect of the molecular weight of the dimethoxyl derivatives of the poly-ethylene oxides on the measured heat of hydration both on (A) weight and (B) molar basis.

ried out in duplicate and the average value calcu-lated. The precision of the experiment was better than 1%. Note that it is well known that these gly-cols exhibit a concentration dependant interaction with water.[1-3,6,7] However, over the very small range of concentrations used in this study, no differences in the measured enthalpies were found when ex-pressed on both a weight and molar basis.
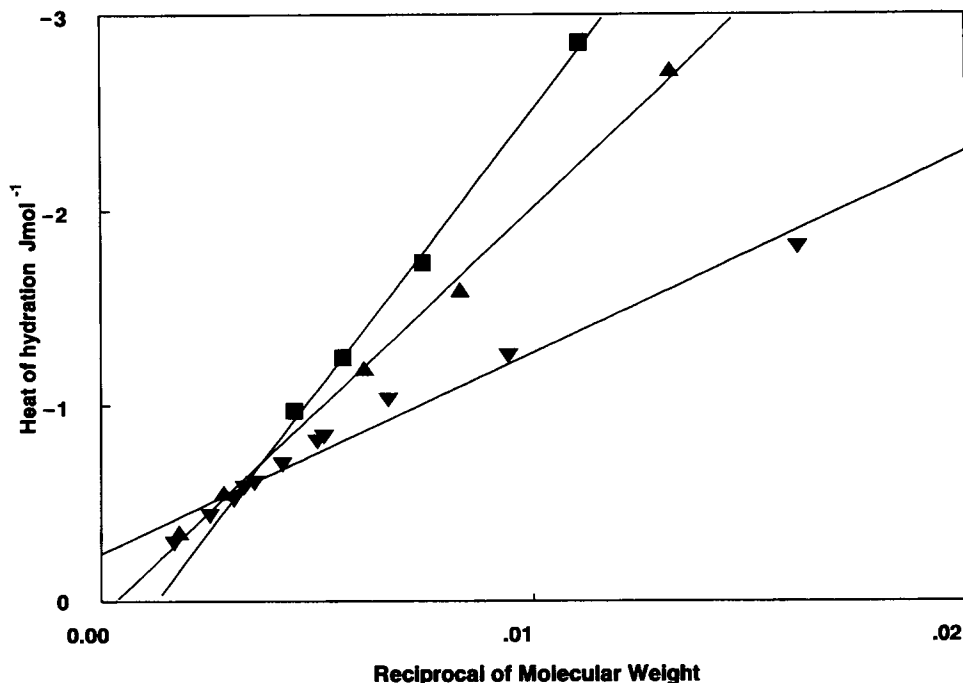
Figure 4 Molar heat of hydration vs. reciprocal of molecular weight for the (▼) oligomeric ethylene oxides and their (▲) monomethoxyl and (■) dimethoxyl derivatives.

RESULTS AND DISCUSSION

Before discussing the results in detail it is important to note that all the experiments were performed using materials in their liquid state in order to eliminate any extra enthalpy changes, for example, heat of solution, an endothermic process, which would occur if the material was a solid.[7]

Oligomeric Ethylene Oxides

Figure 1(A, B) shows the heat of hydration expressed both on a weight and molar basis, respectively, as a function of molecular weight for both the single oligomers and the commercial blends. In both cases the heat of hydration changes rapidly at low molecular weights reaching an asymptote at molecular weights in excess of 400. The equivalence between oligomers and blends of the same average molecular weight suggest that it should be possible to predict blend behaviour from a knowledge of the individual components using the equation:

$$\Delta H_{\text{blend}} = \frac{\sum w_i \Delta H_i}{\sum w_i} \qquad (1)$$

where w_i is the weight of the species with a heat of hydration ΔH_i.

The hypothesis has been tested in two ways; first by investigating binary mixtures of diethylene glycol and tetraethylene glycol and second by using literature molecular weight distributions of both polyethylene glycol 200 and 300 (Table I).[8]

Unfortunately, the latter required values for the heats of hydration of octa-, nona-, and decaethylene glycol: these were extrapolated from Figure 1. For all the binary mixtures and blends there was a close correlation between the observed and predicted heats of hydration (Table II) thus confirming the hypothesis.

Methoxyl Derivatives

Figures 2 and 3 show the heat of hydration (expressed both on a weight and molar basis) as a function of molecular weight for both the monomethyl and dimethyl ethers, respectively. As with the parent compounds, the heats of hydration all decreased with increasing molecular weight reaching asymptotic minima at molecular weights in excess of approximately 400. In addition the data for the commercial blends fell on the same curve as those for the oligomeric.

It is interesting to note that substitution of the end hydroxyl groups by methoxyl increases the measured heat of hydration for the molecule es-

Table III   Results of Regression Analysis for Eq. (2) Using Degree of Polymerisation Instead of Molecular Weight for Molar Heat of Hydration

Polymer	$A \pm SE$	$B \pm SE$	r^2
Parent	0.349 ± 0.051	1.585 ± 0.133	0.9405
Methoxyl derivative	0.224 ± 0.074	2.562 ± 0.140	0.9911
Dimethoxyl derivative	0.409 ± 0.076	2.478 ± 0.127	0.9948

pecially for the lowest molecular weight oligomers. This is believed to be due to the fact that the methyl groups are electron repelling thus giving a greater negative character to the adjacent oxygen and increasing the strength of the hydrogen bond.

CONCLUSION

The effects seen on increasing the molecular weight of both the parent and methoxyl derivatives including the results of the blend are analogous to those seen for the mechanical properties of high polymers such as cellulose acetate,[9] polystyrene,[10] and polypropylene.[11] This would imply that the data should follow the relationship relating a property P to its molecular weight.[12]

$$P = A + \frac{B}{M} \qquad (2)$$

where A and B are constants.

Regression analysis of the data for molar heats of hydration for all three species (Fig. 4) show very high correlations with regression coefficients (r^2) of 0.9729, 0.9973, and 0.9975 for the parent, monomethoxyl, and dimethoxyl derivatives, respectively.

Recently Ogawa[11] has suggested that the B value can be used to compare the difference in the molecular weight dependence among polymer species provided the degree of polymerisation is taken into consideration. It is possible to do this for the materials under test using the generic formula:

$$RO(CH_2CH_2O)_nR.$$
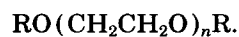
where R is either H- or CH_2-, and appraising the data in terms of n.

If this is done (Table III) then it can be seen that the B values for the two methoxyl derivatives are almost identical but some 60% higher than that for the parent compound. This is interesting because if the measured enthalpy change was dependant solely on the number of bonds formed at the ether linkages without any influence of the end groups, then it would be expected that the B values would be the same for all three species. Obviously the presence of the two hydroxyl end groups does have a significant effect probably due to a change in chain configuration over the methoxyl derivatives. Evidence that the parent polymer in water does not yield coils (as would be expected) but forms a helix has been shown by Maron and Filisko.[7]

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