

Enthalpies of Mixing of Polyoxyethylene Glycols in Benzene, Carbon Tetrachloride, Methyl Alcohol & Ethyl Alcohol

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The enthalpies of mixing (ΔH_m) of polyoxyethylene glycols (mol. wt 4150, 1460, 990, 400 and 200) with benzene, carbon tetrachloride, methanol and ethanol have been determined at 48.2°, employing an isothermal phase-change calorimeter. The temperature dependence of ΔH_m in these solutions indicates that (i) benzene and carbon tetrachloride form complexes with glycols at low temperatures and (ii) polyglycols break the structure of methanol and ethanol.

ENTHALPIES of solution of polyoxyethylene glycols in different non-aqueous solvents at 26.9° have been reported earlier by Lakhanpal *et al.*^{1,2}. Since some of these polyglycol fractions are solids or semi-solids at 26.9°, these authors expressed the enthalpy of solution ΔH_s , as

$$\Delta H_s = \Delta H_t + \Delta H_m/x_2 \quad \dots(1)$$

where ΔH_t represents the lattice energy contribution to ΔH_s , ΔH_m is the heat of mixing of disoriented molecules of the polyglycol and x_2 is the polymer mole fraction. Obviously, the ΔH_t contribution to ΔH_s is much more than that of $\Delta H_m/x_2$, so much so that ΔH_m values could not be determined to any fair amount of accuracy from experimental values of ΔH_s and estimated values of ΔH_t . Since most of the polyglycols exist in liquid state at 48.2° (the temperature at which enthalpies of solution could be determined with an isothermal phase-change calorimeter using cetyl alcohol as the dilatometric fluid)³, the present work has been carried out at this temperature with the object of obtaining unambiguous values of ΔH_m .

Materials and Methods

The different samples of polyoxyethylene glycols (Union Carbide, Canada) had the molecular weights 4150, 1460, 990, 400 and 200. All fractions except the polyglycol of molecular weight 4150 are liquids at 48.2°. The samples were invariably evacuated for 6-8 hr before use in order to remove traces of moisture.

The enthalpies of mixing of the polyglycols with benzene, carbon tetrachloride, methanol and ethanol were determined employing an isothermal phase-change calorimeter^{1,2} in which cetyl alcohol instead of diphenyl ether was used as the dilatometric fluid. A rubber balloon was fastened to the open end of the evacuated stopper of the mixing vessel to prevent any loss of solvent vapour to the atmosphere.

Results and Discussion

In order to present the experimental data on the various systems in a condensed form, the interpolated

values of the heat of mixing $\Delta H'_m = x_2 \cdot \Delta H_s$ at fixed mole fractions of different samples have been reported in Table 1. These values have been reported to the significant number of decimal places to which these can be considered accurate. It may be noticed that the values of $\Delta H'_m$ for solutions of polyglycol of molecular weight 4150 are very much larger as compared to those of the solutions of other fractions at the corresponding mole fractions (x_2). This is on account of the lattice energy contributions to $\Delta H'_m$ in the case of former solutions. The enthalpy of mixing of condensed systems may be expressed by the relation (2) where X_{12} is the number of contacts established between components 1 and 2 on mixing and w is the interchange energy given by Eq. (3).

$$\Delta H'_m = X_{12} \cdot w \quad \dots(2)$$

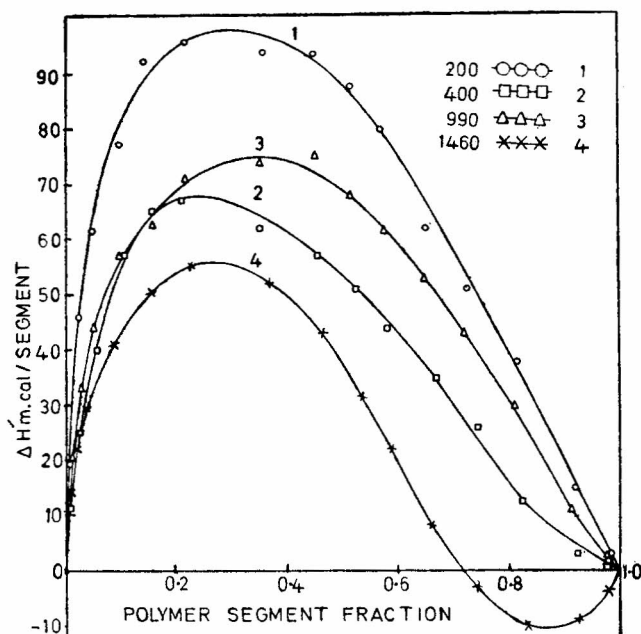
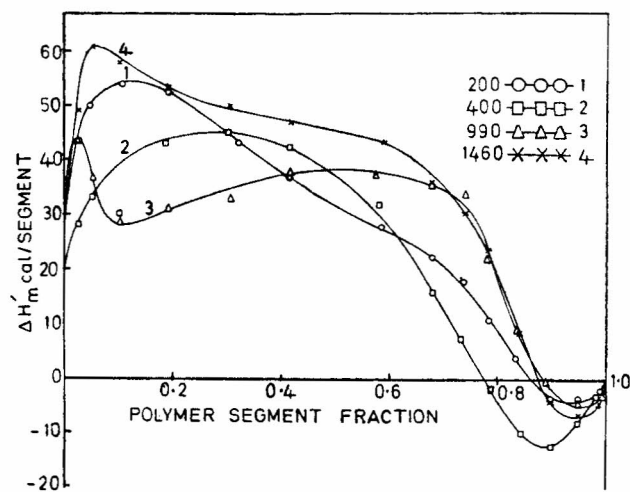
$$w = \epsilon_{12} - 1/2(\epsilon_{11} + \epsilon_{22}) \quad \dots(3)$$

ϵ_{11} , ϵ_{22} and ϵ_{12} in Eq. (2) are the interaction energies of the different types of contacts between molecules

Considering $-(\text{CH}_2-\text{CH}_2-\text{O})-$ to be a common segment in different polyoxyethylene glycol fractions, the values of the enthalpy of mixing ($\Delta H'_m$) per mole of a solution of segments in a solvent were calculated, as plotted in Figs 1 to 4. The relative values of $\Delta H'_m$ (Figs. 1 to 4) of solutions of different polyglycol fractions at a given segment fraction provide a means of ascertaining the dependence of enthalpies of mixing on molecular weight of polyglycol fractions. It may be noticed that $\Delta H'_m$ is generally found to increase with increasing molecular weight of polyglycols except in benzene solutions for which $\Delta H'_m$ decreases with increasing molecular weight of polyglycols. Since for a given segment fraction there are more -OH groups in the same weight of solutions of low molecular weight polyglycols, the dependence of $\Delta H'_m$ for solutions in CCl_4 , methanol and ethanol on molecular weight may be attributed to the relatively strong interactions of the solvent at the -OH sites rather than at the chain oxygen atoms. For benzene solutions the interaction energy of benzene at -OH sites is smaller as compared with that at the chain oxygen atoms. The experimental data have been classified into two groups:

TABLE 1 — HEATS OF MIXING FOR POLYOXYETHYLENE GLYCOL-SOLVENT SYSTEMS

Polymer weight fraction	ΔH_m^* (cal/mole) for polymer fraction					Polymer weight fraction	H_m^* (cal/mole) for polymer fraction				
	4150	1460	990	400	200		4150	1460	990	400	200
BENZENE						METHANOL					
0.05	210	47.5	58.5	56.5	85.0	0.05	120	7.0	7.0	6.0	6.50
0.1	400	71.0	77.5	77.5	111.0	0.1	200	8.50	8.0	7.0	5.0
0.2	920	80.0	109.0	89.0	133.0	0.2	420	14.0	11.0	8.0	6.50
0.3	1480	80.0	128.0	95.0	143.0	0.3	730	22.0	18.0	14.5	11.0
0.4	2180	62.5	136.0	95.0	146.0	0.4	1130	32.0	27.5	22.0	16.0
0.5	3280	30.0	139.0	88.5	135.0	0.5	1900	44.0	38.5	30.5	23.5
0.6	4980	-7.5	138.0	77.5	118.0	0.6	2420	57.5	51.5	39.0	33.5
0.7	7480	-43.5	132.0	62.5	104.0	0.7	—	72.5	64.5	46.0	32.0
0.8	—	-73.5	110.0	45.0	79.0	0.8	—	87.0	79.5	50.0	25.0
0.9	—	-85.0	71.0	25.0	42.5	0.9	—	87.5	83.0	47.5	15.5
CARBON TETRACHLORIDE						ETHANOL					
0.05	420	65.0	33.0	44.0	60.0	0.05	140	11.0	17.0	8.0	11.0
0.1	840	69.0	44.0	61.0	59.0	0.1	250	18.0	18.0	13.0	18.0
0.2	1660	84.0	67.0	68.5	53.0	0.2	515	39.0	39.0	24.0	38.0
0.3	2780	101.0	88.5	64.0	51.5	0.3	855	66.0	66.0	48.0	54.0
0.4	4360	109.0	111.0	37.5	47.5	0.4	1305	98.0	96.0	75.0	66.0
0.5	6220	105.0	95.0	1.0	33.5	0.5	1855	138.0	128.0	107.0	66.0
0.6	2700	37.5	37.5	-37.5	10.5	0.6	2695	182.0	161.0	144.0	81.0
0.7	—	-23.0	-2.0	-62.5	-9.0	0.7	—	230.0	190.0	180.0	90.0
0.8	—	-65.0	-31.5	-62.0	-16.0	0.8	—	300.0	238.0	196.0	87.0
0.9	—	-98.0	-57.0	-45.0	-14.5	0.9	—	328.0	236.0	171.0	60.0

Fig. 1 — Plot of $\Delta H_m'$ versus polymer segment fraction for polyoxyethylene glycol-benzene systemFig. 2 — Plot of $\Delta H_m'$ versus polymer segment fraction for polyoxyethylene glycol-carbon tetrachloride system

(i) Interaction in non-polar solvents and (ii) interaction in polar solvents.

(i) Solutions of liquid polyoxyethylene glycols in benzene² and in carbon tetrachloride¹ have been shown to have significant exothermic heats of mixing at 26.9°. The values of the heat of mixing for these solutions at 48.2° are found to be by and large positive. The observed temperature dependence can be considered as an indication of complex

formation between polyglycol molecules and the solvent molecules, since lower temperatures which favour complex stability result in exothermic contribution to the heat of mixing. This finds ample support from the studies reported by Orye and Prausnitz⁴ who have shown that polar components have a great affinity for aromatic substances which is on account of the formation of charge-transfer complexes. The thermochemical behaviour of a large number of systems⁵, such as, benzene-acetone, benzene-methyl ethyl ketone, paraffins in acetone, aromatic compounds in nitroethane, acetonitrile-acetone, have been shown to have characteristics similar to those of solutions of polyglycols in benzene. It appears, therefore, that the polyglycol-benzene

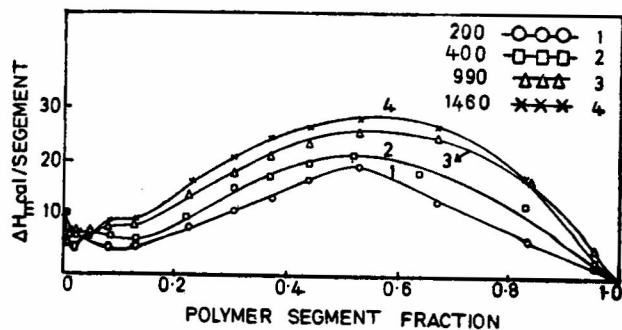


Fig. 3 — Plot of ΔH_m versus polymer segment fraction for polyoxyethylene glycol-methanol system

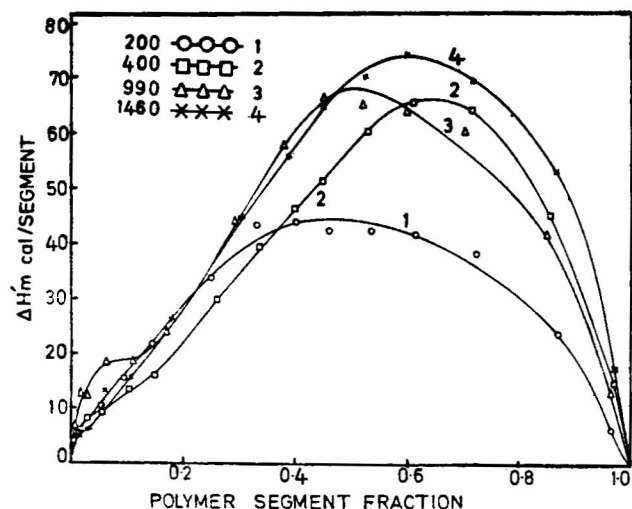


Fig. 4 — Plot of ΔH_m versus polymer segment fraction for polyoxyethylene glycol-ethanol system

interactions involve either dipole-induced dipole interaction or charge transfer complexation.

The exothermic heat of mixing reported for polyglycol-carbon tetrachloride system should not be very surprising since CCl_4 -dioxane mixtures are known to have exothermic heat of mixing⁶, indicating strong interactions between the molecules of the components. It is again found that the CCl_4 -dioxane systems exhibit a positive temperature dependence of ΔH_m . From solid-liquid phase diagrams, Kennard and McCusker⁷ have shown the existence of a compound $\text{C}_4\text{H}_4\text{O}_2 \cdot 2\text{CCl}_4$. Davidson *et al.*⁸ have provided evidence for the formation of charge-transfer complexes between pyridine and CCl_4 . It may, therefore, be assumed that CCl_4

interacts strongly at oxygen sites in the molecules of polyglycols to form charge-transfer complexes.

A perusal of the curves in Figs. 1 and 2 shows that these are far from being symmetrical. The solutions of polyglycols in benzene and carbon tetrachloride tend to show greater endothermicity at concentrations richer in the solvents probably due to the effective rupture of the hydrogen bonding between the molecules of the polyglycols. It may be noticed that for solutions of almost all the polyglycols in CCl_4 , the value of ΔH_m changes sign from positive to negative as the concentration of polyglycols gradually increases.

(ii) It is interesting to observe that for solutions of polyglycols in methanol and ethanol the heat of mixing is invariably positive. This is in conformity with the results reported earlier² for some of the liquid polyglycols at 26.9°. The interaction energy in polyglycols is essentially due to hydrogen bonding. The molecules of methanol and ethanol are known to be hydrogen-bonded. The interactions between dissimilar molecules in alcoholic solutions of the polyglycols are on account of the formation of hydrogen bonds. The positive values of the heat of mixing for alcoholic solutions of polyglycols indicate that the interaction energy ϵ_{12} is numerically smaller than the average value of the interaction energies ϵ_{11} and ϵ_{22} .

It may be observed that unlike the solutions of polyglycols in non-polar solvents, the heat of mixing becomes more endothermic at higher concentrations of polyglycols. This may be attributed to rupture of intermolecular hydrogen bonds in the solvent at high concentrations of polyglycols.

It is interesting to note that the temperature dependence of ΔH_m is not as marked in alcoholic solutions as was found for solutions of polyglycols in non-polar solvents indicating that no complex formation takes place.

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