

Preparation of Water-Soluble Polyurethane Surfactants

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ABSTRACT: A novel series of water-soluble polyurethane surfactants has been prepared by the addition polymerization of 2,4 and 2,6-toluene diisocyanate 80 : 20%, respectively (TDI) to polyethylene glycol (PEG) and/or castor oil and ethylene glycol (EG). These water-soluble polyurethane surfactants have been found to exhibit excellent surface active properties including surface tension, foaming and wetting tendency, and formation of stable emulsions. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1531–1536, 1998

Key words: polyurethane, toluene diisocyanate; polyethylene glycol surfactant; surface tension

INTRODUCTION

A surface-active agent (surfactant) is a substance that, when present at a low concentration in a system, has the property of adsorbing onto the surfaces or interfaces of the system and of altering to a marked degree the surface or interfacial free energies of those surfaces.

The surface active agents have a characteristic molecular structure consisting of a structural group that has very little attraction for the solvent known as a lyophobic group, together with a group that has strong attraction for the solvent called the lyophilic group. This is known as an amphipathic structure, which causes concentration of the surfactant at the surface, reduction of the surface tension of the solvent, and orientation of the molecule at the surface with its hydrophilic group in the aqueous phase and its hydrophobic group oriented away from it.

Many water-soluble polymers, because of their amphipathic structure and surface activity similar to the traditional surfactants, are used as surfactants. For example, the polysorbates exhibit excellent emulsifying properties for oil in water systems^{1,2}; and the polyoxyethylene–polyoxypropylene block copolymers, known by their generic

name as poloxomers, exhibit surface properties, such as emulsion stabilization, dispersion, and demulsification.³

This article describes the preparation and surface active properties of a series of novel water-soluble polyurethane surfactants. The surface active properties studied in this article include surface tension, foaming tendency, formation of stable emulsion, and wetting power.

EXPERIMENTAL

Preparation of Water-Soluble Polyurethane Surfactants

In a $\frac{1}{2}$ L four-necked flask equipped with a mechanical stirrer, a thermometer, a reflux condenser, and a dropping funnel, the calculated quantities of PEG and/or castor oil were mixed well with 100 cm³ acetone. The temperature was adjusted at 50°C \pm 3. The calculated quantity of TDI was dropped slowly in a period of 1 h while stirring was continued, and 0.01% (of solid matter) of dibutyltin dilaurate was added as a catalyst.

The whole mixture was stirred for 3 h, the calculated quantity of EG was then added, stirring was continued for 1 h, then the product was poured into a petri dish. After acetone solvent was evaporated, a solid, rubber-like, opaque, and com-

Table I Ingredients of Preparation of Polyurethane Surfactants

Compound	PEG 6000, Equivalent	PEG 4000, Equivalent	Castor Oil, Equivalent	TDI, Equivalent	EG, Equivalent
I	0.2	—	—	0.3	0.2
II	0.1	—	0.1	0.3	0.2
III	—	0.2	—	0.3	0.2
IV	—	0.1	0.1	0.3	0.2

pletely water-soluble polyurethane surfactant was formed.

Analysis

- Acid values and hydroxyl values were determined and, from these values, the average molecular weights of water-soluble polyurethanes were calculated⁴ (Table I).
- Infrared (IR) spectra were obtained with Fourier transform (FTIR) spectrometer, ATI Mattson Genesis Series (Figs. 1 and 2).

Measurements

1. Surface tension was measured by a Du Nouy tensiometer, KRUSS type 8451.

2. Foaming was measured according to Camps and Durham.⁵

3. Emulsion stability was measured according to Takeshi,⁶ in which 10 g of 0.1M surfactant in water was mixed well with 10 g of paraffin oil. Water should be separated gradually from the emulsion, and the time and quantity of separated water should be quoted.

4. Wetting was measured according to Draves.⁷

RESULTS AND DISCUSSIONS

Preparation

The preparation of water-soluble polyurethanes can be represented as shown in Scheme 1; the

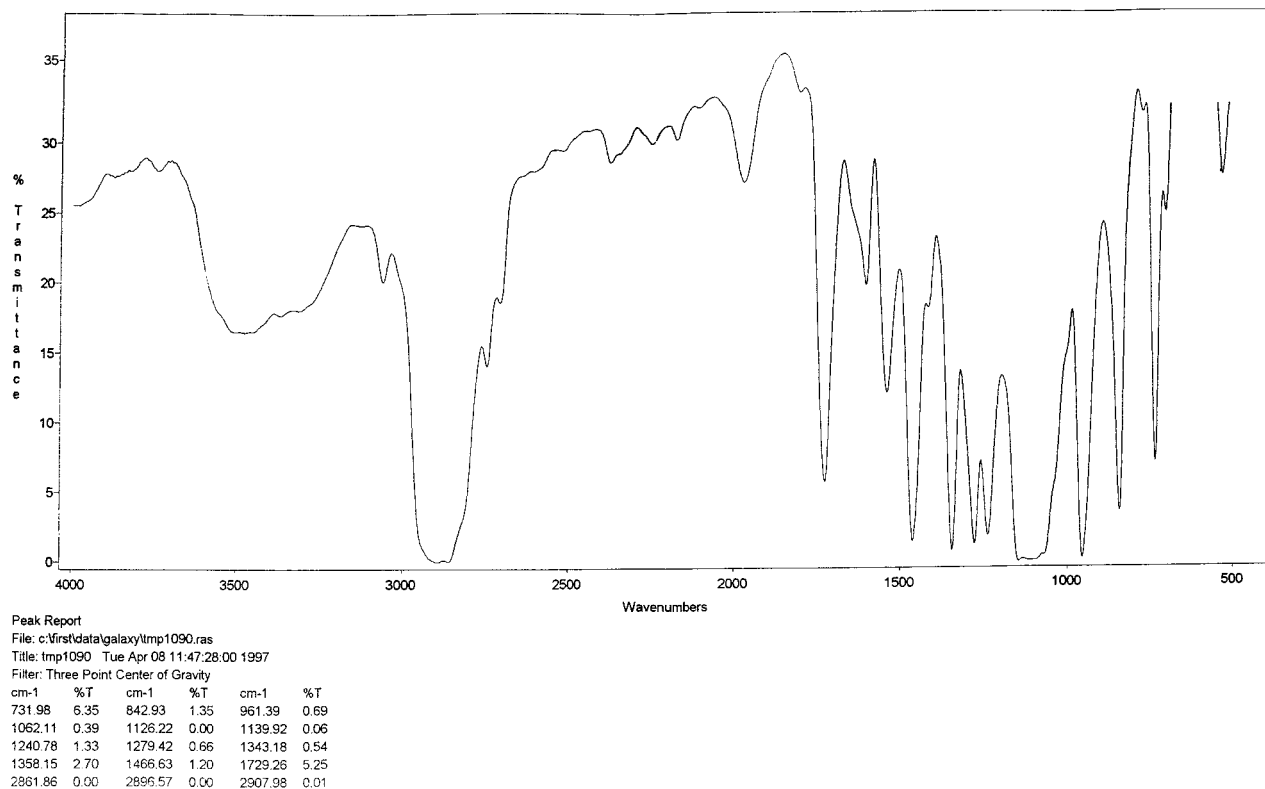


Figure 1 IR analysis of compound I polyurethane surfactant.

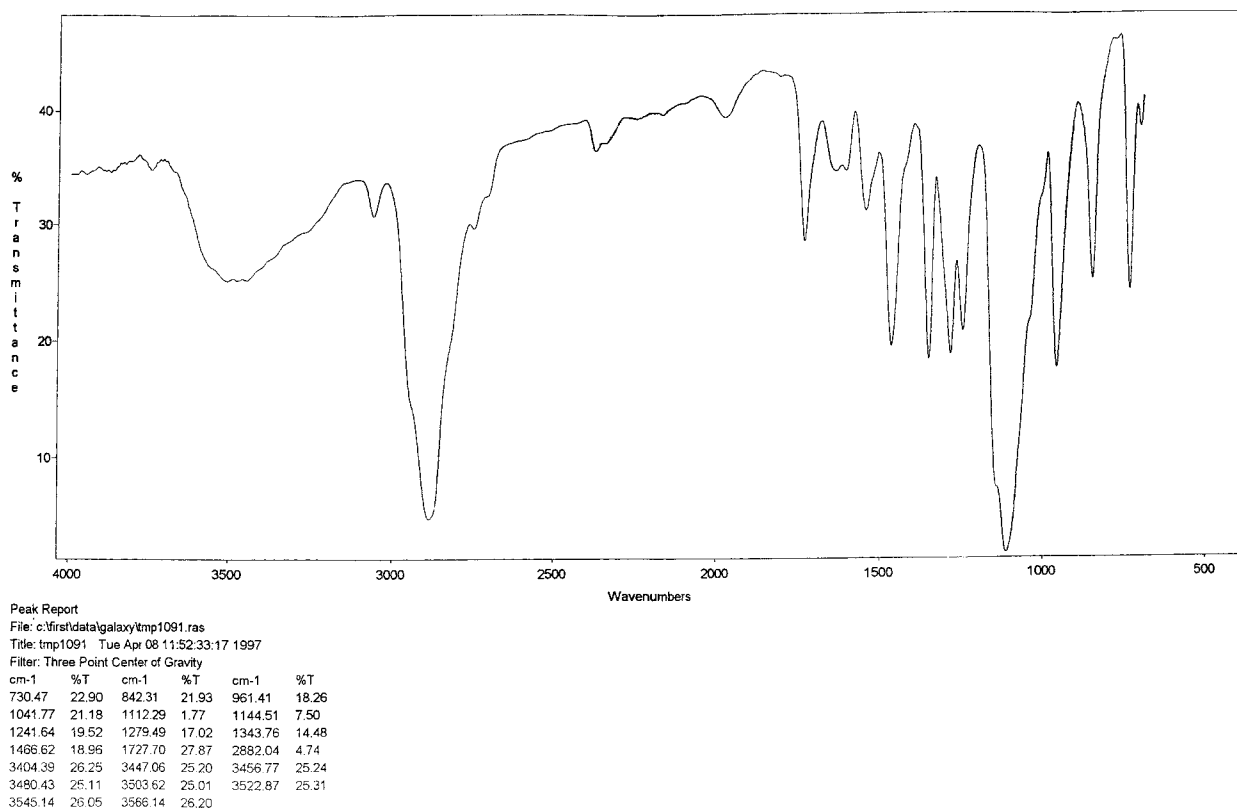
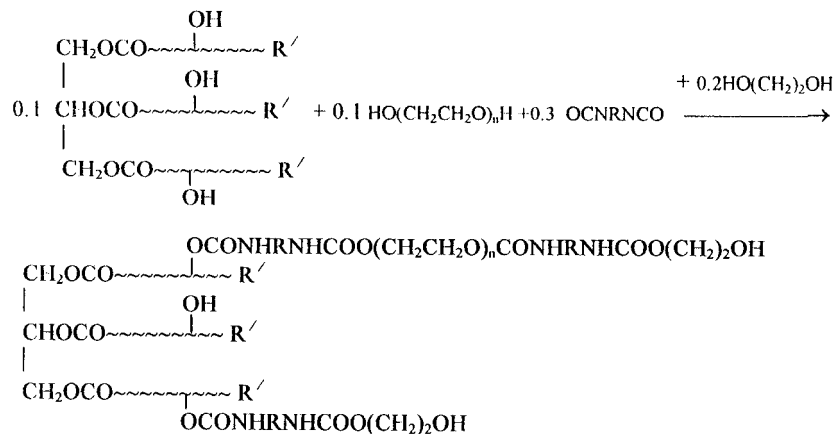
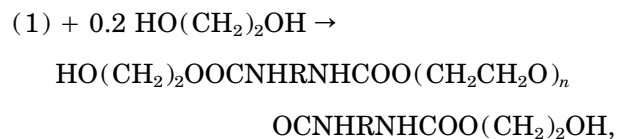
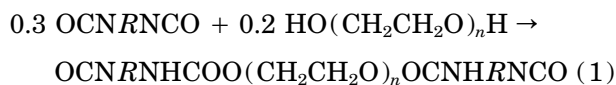


Figure 2 IR analysis of compound II polyurethane surfactant.

analysis is shown in Table II; and the IR of compounds I and II are shown in Figures 1 and 2, respectively.

where *R* is the toluene portion, and *n* denotes the polyoxyethylene glycol portion of 6000 or 4000. Step 2:

Scheme 1 includes the following two steps. Step 1:



Scheme 1 Water-soluble polyurethane surfactant, (compounds II or IV), where *R'* is the fatty acid portion of castor oil.

Table II Analysis of Water-Soluble Polyurethane Surfactants

Compound	Acid Value	Hydroxyl Value	Average Molecular Weight	Hydrophilic (%)	Hydrophobic (%)
I	4.8	4.4	12180	95.87	4.13
II	4.7	4.44	12420	84.28	15.72
III	6.2	6.08	9140	93.96	6.04
IV	6.02	5.91	9390	78.31	21.69

water-soluble polyurethane surfactant, (compounds I or III).

In the case of using castor oil, the two steps can be represented in Scheme 1.

SURFACE TENSION

Water-soluble polyurethane surfactants prepared in this study are observed to be of an amphipathic structure similar to the traditional surfactants in which the aromatic residue and/or castor oil residue is the hydrophobic portion and the oxyethylene units (non ionic) are the hydrophilic portion.

The surface activity of these water-soluble polyurethane surfactants (surface tension versus molar concentration) are shown in Figure 3. It is clear that the surface tension of the solutions is reduced relatively by the addition of the surfactants. It is due to the amphipathic structure of

the surfactant molecule, which causes its concentration at the surface, reduction of the surface tension, and orientation of the molecules at the surface with its hydrophilic (oxyethylene) groups in the aqueous phase and its hydrophobic groups (aromatic and/or castor oil residues) oriented away from it.

An increase in the length of the polyoxyethylene chain results in a decrease of surface activity. This is due to the increase of the hydrophilic centers of a surfactant, which causes the concentration of the molecules at the surface to decrease and, consequently, the decrease of its surface tension.⁸ On the reverse of this, the incorporation of additional hydrophobic portion (castor oil portion) in the surfactant molecule causes an increase in its efficiency as a surfactant.

The inflection point has been observed in the curves. The concentration at the inflection point corresponds to the critical micelle concentration

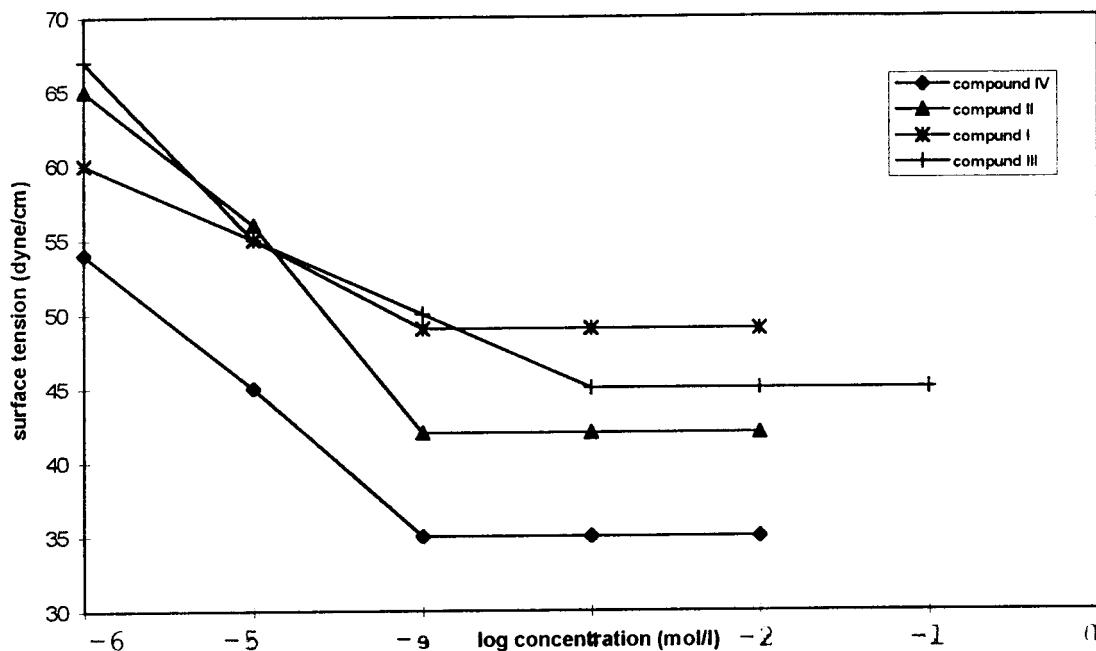


Figure 3 Plots of surface tension against molar concentration for water-soluble polyurethane surfactants.

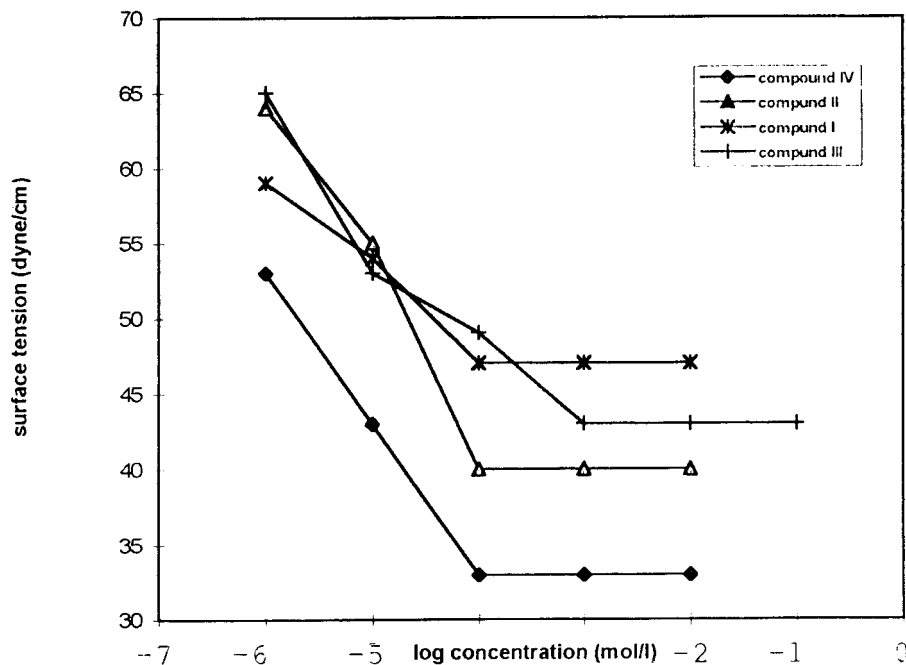


Figure 4 Plots of surface tension against log molar concentration for water-soluble polyurethane surfactants in 0.1M NaCl solution.

(CMC) in the cases of traditional surfactants. The values are found smaller than that of traditional surfactants due to the high molecular weight and larger hydrophobic chain of water-soluble polyurethane surfactants.

The effects of electrolyte addition on the surface activity of water-soluble polyurethane surfactant solutions are shown in Figure 4. It was found that the addition of 0.1M of NaCl to surfactant solutions increases surface activity (that is, a decrease of surface tension versus concentration), and this is due to the fact that electrolyte decreases the repulsion between the oriented^{9,10} ionic hydrophilic ($\text{CH}_2\text{CH}_2\text{O}$) heads results in closer packing at the surface layer as the ionic strength is increased.¹¹

FOAMING

Absolute liquids do not foam. Foam is produced when air or some other gas is introduced beneath

Table III Foaming Properties of Polyurethane Surfactants

Compound	Height (cm)	Time Stability (min)
I	4	4.5
II	6	6
III	3.5	4
IV	4.8	5

the surface of a liquid that expands to enclose the gas with a film of liquid (Table III).

Foam height and foam stability reach a maximum at certain oxyethylene chain length and then decrease. This is due to Van der Waals forces between surfactant molecules decrease with increasing oxyethylene content since the area per molecule at the surface increases with this change. On the other hand, the polyoxyethylene chain is believed to be coiled in the aqueous phase,¹² and the cohesive forces due to intra- and intermolecular hydrogen bonding are stated to pass through a maximum with increasing oxyethylene content. The summation of the Van der Waals and hydrogen-bonding cohesive forces consequently passes through a maximum as the oxyethylene content of the molecule is increased.

Compounds II and IV give higher foam than compounds I and III, and this is due to the hy-

Table IV Stability Properties of Polyurethane Emulsion

Type	Quantity of Separated Water (g)	Time (h)
Compound I	7	72
Compound II	5.5	72
Compound III	6.5	72
Compound IV	5	72

drophobic (castor oil) portion is believed to diffuse rapidly to the interface, and the interchain cohesion is increased.¹² At the same time, these compounds (II and IV) give appreciable stable foams because of the above reasons and should require an interfacial film with sufficient cohesion to impart elasticity and mechanical strength to the liquid lamellae enclosing the gas in the film.

EMULSION STABILITY

In this study, the polyurethane emulsifying agent gives a stable emulsion with paraffin oil for a certain time, according to the structure of the polyurethane (Table IV).

The formation of emulsion is due to the fact that the hydrophobic groups are facing the oil phase and the hydrophilic groups are facing the aqueous phase. So it is important that surfactant should contain sufficient hydrophobic groups to permit a large degree of solubilization of the oil phase necessary to produce an emulsion, and the extent of the solubilized paraffin oil increases in formulas II and IV, which contain more hydrophobic groups (castor oil portion). The remaining water was dispersed in the oil phase to give water in oil emulsion, which was stable above 4 months in all types of emulsions.

Wetting	
Surfactant	Wetting Times (s)
Compound I	36
Compound II	25
Compound III	28
Compound IV	19

The addition of the polyurethane surfactant to water causes the adsorption of the surfactant at the substrate-liquid interface, and the amphipathic surfactant molecules are oriented with their polar groups toward the water and their hydropho-

bic tails toward the substrate. So the rate of wetting is a function of the surface tension, and, thus, surfactants having more hydrophobic groups (such as compounds II and IV) are generally believed to have faster rates of diffusion to, and orientation at, surfaces than those with low hydrophobic groups (such as compounds I and III).

CONCLUSIONS

A novel series of water-soluble polyurethane surfactants has been prepared by the addition polymerization of TDI to PEG and/or castor oil. Because of the unique structure features of these surfactants, high molecular weight, aromatic and/or castor oil residues of hydrophobic portion, and polyoxyethylene chains of hydrophilic portion, these surfactants have been found to exhibit excellent surface active properties, including surface tension, foaming and wetting tendency, and formation of stable emulsions.

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