M. P. ZVEREV, S. P. RUCHINSKII, P. I. ZUBOV

The integral thermal effect of dissolution is the algebraic sum of three quantities

1963

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

M. P. ZVEREV, S. P. RUCHINSKII, P. I. ZUBOV

DEPENDENCE OF THE THERMAL EFFECTS OF POLYMER DISSOLUTION ON THE NATURE OF THE SOLVENT

(Presented by Academician V. A. Kargin, August 20, 1962)

The integral thermal effect of dissolution is the algebraic sum of three quantities

$$Q = -E_{11} - E_{22} + 2E_{12}, \tag{1}$$

where E_{11}, E_{22}, and E_{12} are the interaction energies of solvent molecules, polymer molecules, and solvent molecules with polymer molecules.

By comparing experimental data on heats of dissolution and swelling with the properties of dilute and concentrated polymer solutions, it was established in this work that in equation (1) it is necessary to take into account the process of formation of new local bonds between the links of macromolecules.

The objects of study were divinylstyrene (SKS-30A) and divinylnitrile (SKN-26) copolymers. As solvents, substances of different chemical nature were taken, which had been used previously (1). The thermal effects of polymer dissolution were studied in an adiabatic calorimeter (2) at 25°. The densities of the polymer–solvent systems were determined by the gradient-tube method, based on comparison of the density of the substance with the density of a liquid (3).

Table 1

Thermal effects of dissolution and characteristic viscosity of SKS-30A and SKN-26 copolymers in various solvents

Name of solvent	Dipole moment, D	SKS-30A: heat of dissolution, cal/g	SKS-30A: characteristic viscosity	SKN-26: heat of dissolution, cal/g	SKN-26: characteristic viscosity
Ditolylmethane	1.33	−0.56	2.31	+0.92	1.98
Dicumylmethane	1.38	−0.45	2.12	+0.14	swells to a limited extent

Name of solvent	Dipole moment, *D*	SKS-30A: heat of dissolution, cal/g	SKS-30A: characteristic viscosity	SKN-26: heat of dissolution, cal/g	SKN-26: characteristic viscosity
Dibutyl sebacate	2.44	−0.16	1.32	−0.17	1.22
Dibutyl phthalate	2.88	−0.65	swells to a limited extent	+0.17	2.21

Table 1 gives data on the heats of dissolution and characteristic viscosity of the SKS-30A and SKN-26 copolymers in various solvents.

It is evident that, on the basis of equation (1), one would expect that, with an increase in the dipole moment of the solvent, the thermal effect of dissolution of the nonpolar divinylstyrene copolymer should decrease. Meanwhile, as follows from the experimental data, it increases. In our opinion, the relative increase in the thermal effect of dissolution of SKS-30A with increasing polarity of the solvent is connected with the fact that in these

under these conditions the number of local bonds between the units of the macromolecules increases*.

Further, from the data in Table 1 it is seen that the maximum heat effect is observed upon dissolution of the polar polymer SKN-26 in the slightly polar ditolylmethane; in more polar solvents (dibutyl phthalate and dibutyl sebacate) the heat effect is considerably smaller, which also does not follow from equation (1). It should be noted that the limited swelling of the divinylnitrile polymer in dicumylmethane is also accompanied by the evolution of heat, which indicates an increase in the number of polar bonds between units of the polymer chain.

Table 2

Density of polymer-solvent systems

Polymer name	Solvent name	Concentration, wt. % polymer	Concentration, wt. % solvent	Additive density, g/cm^3	Experimental density, g/cm^3	Contraction, Δv
SKS-30A	Ditolylmethane	74	26	0.9341	0.9295	−0.0053
SKS-30A	Dicumylmethane	82	18	0.9234	0.9210	−0.0028
SKS-30A	Dibutyl sebacate	82	18	0.9227	0.9224	−0.0004

Graph of the dependence of the transition temperature to the viscofluid state of the divinylnitrile polymer SKN-26 on the nature of the plasticizer.

Figure 1: Graph of the dependence of the transition temperature to the viscofluid state of the divinylnitrile polymer SKN-26 on the nature of the plasticizer.

Polymer name	Solvent name	Concentration, wt. % polymer	Concentration, wt. % solvent	Additive density, g/cm^3	Experimental density, g/cm^3	Contraction, Δv
SKS-30A	Dibutyl phthalate	82	18	0.9405	0.9350	−0.0063
SKN-26	Ditolylmethane	82	18	0.9657	0.9707	+0.0053
SKN-26	Dibutyl sebacate	80	20	0.9569	0.9631	+0.0061
SKN-26	Dibutyl phthalate	82	18	0.9768	0.9810	+0.0044

As is seen from the data of Table 1, for the nonpolar polymer SKS-30A there is a dependence between the dipole moment of the solvent, the heat effect of dissolution, and the characteristic viscosity of the solution. In our opinion, this is determined by the fact that in nonpolar polymers all bonds are equivalent, and with an increase in the dipole moment of the solvent the polymer macromolecules in solution become more coiled. When a polymer containing polar groups (SKN-26) is dissolved, such a regularity is absent, which is apparently caused by a more complex redistribution of bonds between the polar and nonpolar groups of the macromolecules when the dipole moment of the solvent changes.

The same redistribution of bonds between the polar and nonpolar groups of the macromolecules of the divinylnitrile copolymer in different solvents is also manifested when the density of concentrated solutions of this polymer is studied. Thus, from the data of Table 2 it can be seen that the greatest value of contraction, indicating the greatest coiling of the chains, is observed when SKN-26 is dissolved in dibutyl sebacate.

Fig. 1. Dependence of the temperature of transition to the viscofluid state of the divinylnitrile polymer SKN-26 on the nature of the plasticizer.
a —dicumylmethane, *b* —ditolylmethane, *v* —dibutyl phthalate, *g* —dibutyl sebacate

In ditolylmethane the contraction is greater than in dibutyl phthalate, but less than in dibutyl sebacate.

* The only exception is the solution of this polymer in dibutyl phthalate, which is apparently due to the limited swelling of SKS-30A in dibutyl phthalate.

The change in contraction in solutions of the divinylstyrene copolymer occurs symbatically with the change in the heats of dissolution and the characteristic viscosity when the polarity of the solvent is changed.

On the basis of the data presented, we arrive at the conclusion that, in studying the heats of dissolution and swelling of polymers, it is necessary to take into account the formation of new bonds between the units of macromolecules in solution. In this case the integral thermal effect of dissolution will be determined by the following equation:

$$Q = -E_{11} - E_{22} + 2E_{12} + E'_{22}, \tag{2}$$

where E'_{22} is the energy of the newly formed local bonds between units of macromolecules in the polymer solution.

The nature of the interaction of the solvent (plasticizer) with the polymer also affects the flow temperature of the polymer.

Thus, from Fig. 1 it is seen that when divinylnitrile polymer is mixed with ditolylmethane, dibutyl sebacate, and dibutyl phthalate, the flow temperature decreases as the concentration of the plasticizer increases.

When this polymer is mixed with dicumylmethane, however, nonmonotonic changes in the flow temperature are observed. In the region of small additions (up to 1.5%) of plasticizer, the flow temperature of the swollen polymer is higher than in the initial polymer; at larger additions of plasticizer, the flow temperature decreases, as it does in the presence of other substances.

These data, as it seems to us, are of definite interest in connection with the problem of polymer plasticization and fiber production.

Moscow Institute of Fine Chemical Technology
named after M. V. Lomonosov
Institute of Physical Chemistry
Academy of Sciences of the USSR

Received
20 VIII 1962

CITED LITERATURE

[1] M. P. Zverev, P. I. Zubov, *Koll. zhurn.*, **22**, 756 (1960). [2] S. M. Skuratov, *Koll. zhurn.*, **9**, 133 (1947). [3] N. V. Mikhailov, V. O. Gorbacheva, N. N. Zav' yalova, *Khim. volokna*, No. 1 (1960).

Note: Figure translations are in progress. See original paper for figures.