

## **Thermodynamics of Macromolecular Systems**

### **2. Light Scattering Measurements Polystyrene-Cyclohexane-Acetone**

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#### **SUMMARY**

From light scattering measurements in the system polystyrene-cyclohexane-acetone within the temperature range from 288 to 323 K it is concluded that the surface of the reduced chemical potential of the solvent as function of solvent composition and temperature exhibits the characteristics of true cosolvency. The influence of cyclohexane-acetone ratio on the temperature dependence of the corresponding enthalpy and entropy parameters is discussed. The cosolvency effects are evidenced also by studies of the STAUDINGER index at 34.5<sup>0</sup> C over the whole range of the ternary system.

Properties of the binary solvent mixture cyclohexane-acetone, i. e. excess volume and viscosity, indicate that acetone clustering breaks down by dilution with cyclohexane. Consequently, the observed true cosolvency may be interpreted as caused by the combined action of cyclohexane and non-associated acetone.

#### **INTRODUCTION**

In the course of the aim to interpret effects of polymer miscibility it has been proposed in the foregoing paper (CANTOW, H.-J. and SCHUSTER, R. H., 1982) to substitute macromolecules by low molecular weight representative models (LMWM) as far as possible: Concerning the energetic part of miscibility the situation is analogous for the macromolecular chains and its LMWM's. Dispersive and specifically interacting subunits yield competing contributions. Such a LMWM may be identical with repeating units of the polymer. Alternately a mixture of two low molecular weight compounds, one of them of the dispersive, the other of the specifically interacting type, may simulate the situation within the macromolecular chain. From the surface of the reduced thermodynamic parameters of the solvent as function of solvent composition and temperature, as derived from solution or from swelling data, mixed systems with optimal solution properties may be derived. This knowledge may be transduced to the macromolecular scale.

Thus copolymers may be designed, which are optimal partners for another polymer with respect to miscibility. In the present paper a first step into this direction is presented by reporting light scattering measurements in the ternary system polystyrene-cyclohexane-acetone, both the latter components simulating a copolymer built up by dispersive and by specifically interacting subunits.

Some pioneering work on solution thermodynamics in ternary systems, with special reference to systems containing acetone, may be reported first. PALIT, COLOMBO and H. MARK (1951) have noticed cosolvency of polystyrene in acetone-methylcyclohexane mixtures. Both partners are non-solvents for polystyrene at room temperature. LANGE (1965) has studied preferential solvation of macromolecules by combining light scattering and refractive index increment experiments. The type of solvation around the chain backbone had been evaluated applying the theoretical approach of STRAZIELLE and BENOIT (1961). WOLF et al. (1973, 1978) have investigated polystyrene in acetone-diethylether solutions. The mixture of a non-solvent and of a partly solving component turned out to be a thermodynamically good solvent. They indicate such effects as "true cosolvency". According to WOLF it is not necessary that preferential solvation occurs at different sites in the macromolecule by action of both the components. He claims that a certain "incompatibility" of the solvent components suffice to explain true cosolvency. He recommends to apply mixed solvents in order to tailor certain thermodynamic conditions. Three types of mixed solvents are distinguished according to WOLF, with the characteristics: 1. Monotonous change of the solvent quality, 2. positive deviation -true cosolvency- and 3. negative deviation -co-non-solvency-. Polystyrene-cyclohexane-dimethylformamide is quoted as an example for the latter case. Furthermore, WOLF and BLAU have communicated some studies concerning the influence of pressure on true cosolvency (1976).

## RESULTS AND DISCUSSION

1949 SCOTT has suggested to reduce three-component solution systems to binary ones: Polymer plus a hypothetical single liquid of average properties. This single liquid approximation may be helpful in the study of the global solvent effect caused by the binary solvent mixture. The results may be compared easily without complicating the explicit expressions for the second virial coefficients.

The relation derived by YAMAKAWA (1967) between apparent molecular weight,  $\bar{M}_{w\text{ app}}$ , apparent second virial coefficient,  $A_{2\text{ app}}$  and the true quantities,  $A_2$  and  $\bar{M}_w$

$$A_2 = A_{2\text{ app}} \cdot \bar{M}_{w\text{ app}} / \bar{M}_w \quad (1)$$

was tested with good results in mixed solvents, where strong selective adsorption

occurs (COWIE, J. M. G., 1968 and OKITA, K. et al., 1968).

Thus, with known  $\bar{M}_w$ ,  $A_2$  can be calculated from the slope of equation (2)

$$c_2/R_{90} = (c_2/R_{90})_{c \rightarrow 0} + 2(c_2/R_{90})_{c \rightarrow 0} \cdot \bar{M}_w \cdot A_2 \cdot c_2 \quad (2)$$

The reduced thermodynamic solution parameters of the solvent have been calculated according to REIK and GEBERT (1954) and CANTOW (1956)

$$\frac{\Delta\mu_1^e}{c_2 \bar{v}_1} = -B \quad \frac{\Delta h_1}{c_2 \bar{v}_1} = T \frac{\partial B}{\partial T} - B \quad \frac{\Delta s_1^e}{c_2 \bar{v}_1} = \frac{\partial B}{\partial T} \quad (3)$$

The light scattering measurements were carried out at right angle, using a photometer especially designed by KOWALSKI and CANTOW for use over a broad range of temperatures, down to  $-50^\circ\text{C}$ , with a linear polystyrene,  $M_w = 5.1 \times 10^4$  and  $\bar{M}_w/\bar{M}_n = 1.02$  (WATERS). Sealed cuvettes were used for the solutions.

The values of the reduced chemical potential of the solvent derived from light scattering are presented in Figure 1, as a function of the acetone mole fraction,  $x_2$ , and the temperature. It is evident that the influence of the solvent mixture dominates that of the temperature with respect to the solution properties of polystyrene. All isothermes behave non-ideal. The analytical expression of the concentration dependence of the reduced chemical potential of the solvent is complicated. However, it is evident that the chemical potential surface exhibits a deep minimum valley intersected by the plane  $x_2 = .5$ . The mixture of the solvent cyclohexane with the non-solvent acetone forms a structure with much better solvation properties than cyclohexane, irrespective the temperature. Points are indicated in Fig. 1 at the intersections of the reduced chemical potential surface with the plane  $\Delta\mu_1^e/c_2 \bar{v}_1 = 0$  and with the corresponding projection in the plane  $\Delta\mu_1^e/c_2 \bar{v}_1 = .9$ . The curves through these two groups of points indicate the existence of a lower critical temperature for the ternary system polystyrene-cyclohexane-acetone, which is situated in the concentration range  $.45 < x_2 < .55$ . At  $x_2$  values above  $.5$  it is obvious that minor changes in  $x_2$  induce large changes of the  $\Theta$ -temperature, whereas below  $x_2 \approx .5$  - in a rough approximation - the  $\Theta$ -temperature changes  $10^\circ$  with  $x_2$  changes of  $.1$ .

The temperature dependence of the reduced chemical potential is a function of the acetone concentration (Figure 2). The T-dependence of  $\Delta\mu_1^e/c_2 \bar{v}_1$  determines that of the thermodynamic dilution functions  $\Delta h_1/c_2 \bar{v}_1$  and  $T\Delta s_1^e/c_2 \bar{v}_1$ . Figure 3 presents composition and temperature dependence of the thermodynamic solution parameters. The points at which  $\Delta h_1$  and  $-T\Delta s_1^e$  cancel are the pseudoideal states. Below 308 K there are two such points on each isotherm, which limit the region of

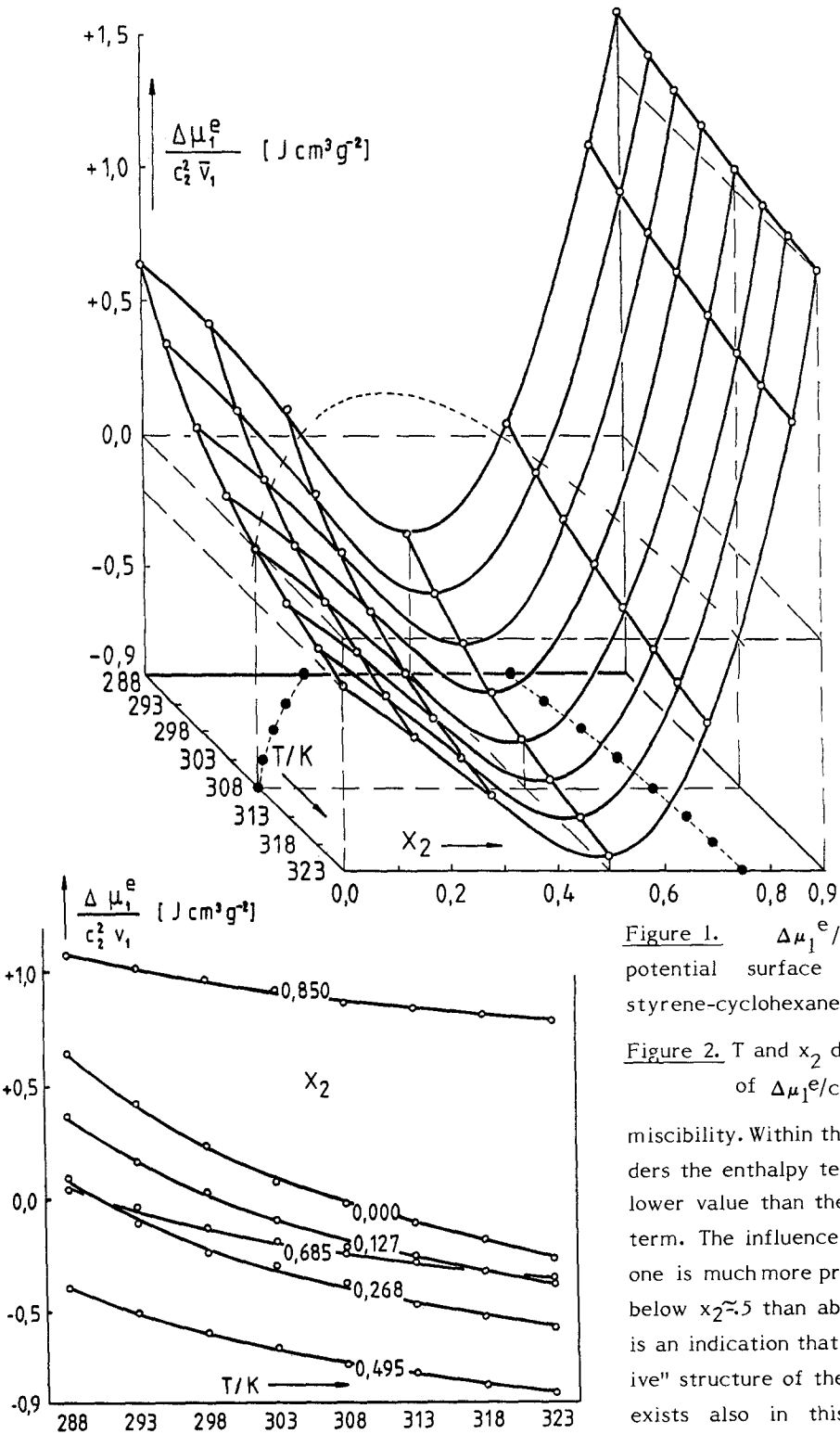


Figure 1.  $\Delta\mu_1^e/c_2^2 v_1$ , potential surface poly-styrene-cyclohexane-acetone

Figure 2. T and  $x_2$  dependence of  $\Delta\mu_1^e/c_2^2 v_1$

miscibility. Within these borders the enthalpy term has a lower value than the entropy term. The influence of acetone is much more pronounced below  $x_2 \approx 0.5$  than above. This is an indication that the "active" structure of the mixture exists also in this region

From Figure 3 a solvent effect is evident which can be expressed qualitatively as  $\partial\Delta h_1/\partial x_2$  and  $\partial\Delta s_1/\partial x_2$ . This specific solvent effect exhibits its maximum value at  $x_2 = 0$  for both functions. The slope  $\partial\Delta s_1^e/\partial x_2$  becomes progressively weaker with increasing acetone concentration. Such changes may have its origin in orientation effects due to the "active" structure of the mixture, which is formed by the dilution of acetone with cyclohexane. It is remarkable that the enthalpy term passes through a minimum endothermic state at  $x_2 \approx .5$  and rises slowly than towards higher acetone concentrations. The endothermic minimum evidences that here the interaction with the solute has the maximum values.

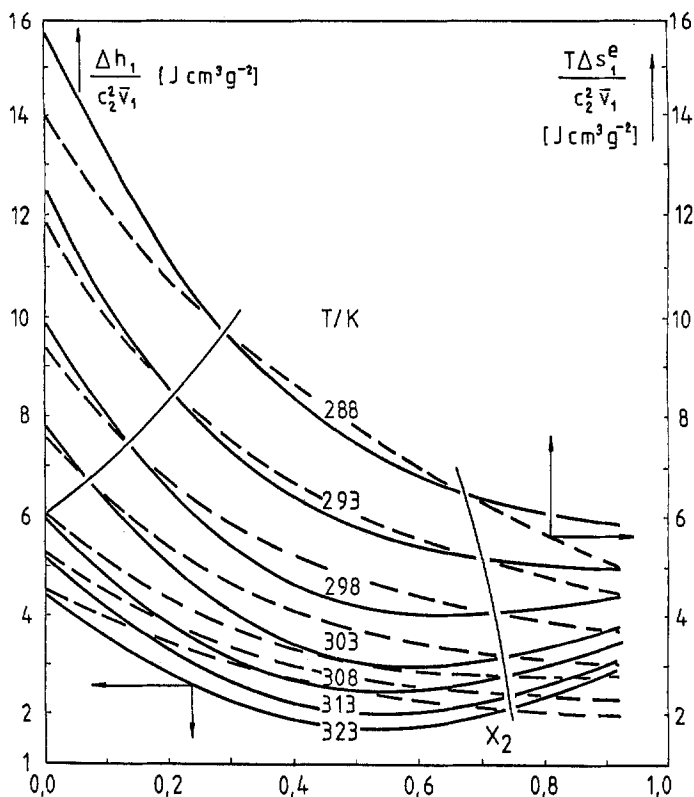


Figure 3. Reduced enthalpic and entropic functions at  $x_2 \approx .5$  and rises slowly than towards higher acetone concentrations. The endothermic minimum evidences that here the interaction with the solute has the maximum values.

In the following an attempt is made to interpret the increasing solvent activity of acetone with decreasing  $x_2$  by means of studies on the pure solvent mixture.

A significant positive excess volume has been found for cyclohexane-acetone mixtures within the whole temperature range, 288 - 323 K (see Figure 4) (SCHUSTER, R. H. and CANTOW, H.-J., to be published). Such a behaviour can occur in mixtures of non-polar molecules of different size and shape, as well as in mixtures in which one component associates in the pure state. Association is broken off than by dilution with the unpolar component. The maximum of  $\Delta V^e$  is situated at  $x_2 \approx .5$  again. As demonstrated in Figure 5 the mixtures of cyclohexane and acetone exhibit non-ideal behaviour. These observations - volume and viscosity non-ideality - support the plausible assumption that association -clustering- of acetone molecules breaks down by dilution with cyclohexane.

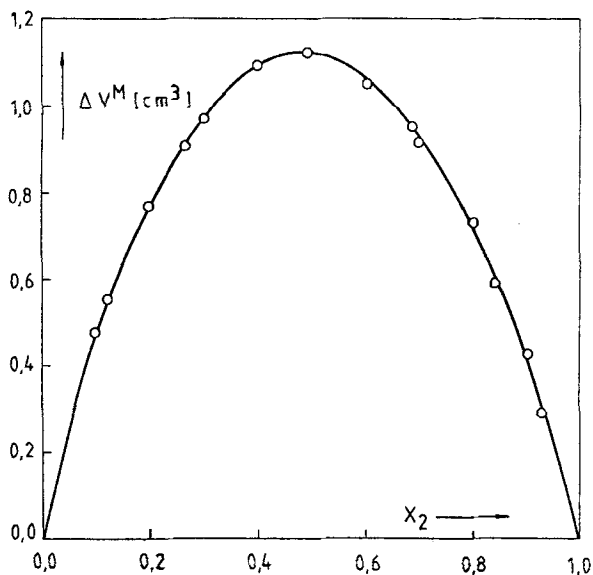


Figure 4. Excess volume of cyclohexane-acetone mixtures, 300 K

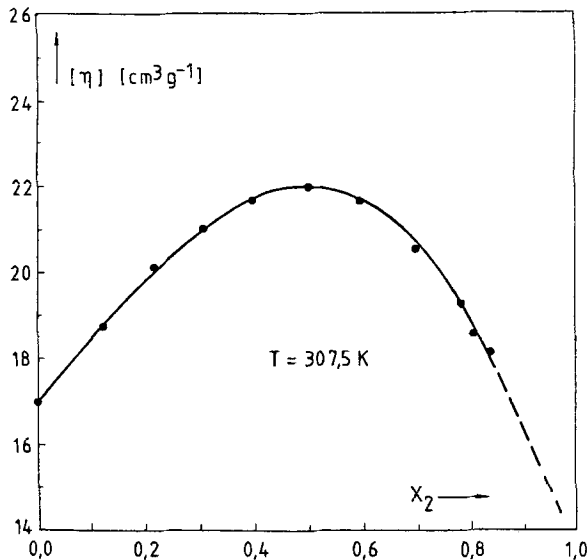


Figure 7. Viscosity  $\eta$ , 307,5 K, and non-ideality term  $(\eta^M - \eta^{id}) / \eta^{id}$  cyclohexane-acetone

Consequently, the free energy of the "specific" polar component of the mixture is higher in the composition range  $0 < x_2 < .5$  than in the pure solvent. Thus, interactions between the "specific" component and the solute, polystyrene, can determine a pronounced decrease of the free energy of the "specific" component. This contributes to an enhanced solubility of polystyrene. The deep minimum of the chemical potential is caused by the maximal concentration of the specifically interacting species.

If this is true, the degree of dissociation of the acetone can be approximated. It has to be assumed that a fraction of the acetone molecules is clustered in the pure liquid. Even if the breakdown of the association is not complete at  $x_2 = 0$  the maximal dissociation is reached here. The exothermic contribution of the dissociated acetone, the active specific component, can be attributed to be the intercept of  $x_2 = 1$  axis and a tangent at  $x_2 = 0$  on the  $\Delta h_1^e / c_2^2 v_1$  curve. From this intercept at

a given temperature and from the acetone concentration in the system the approximate degree of dissociation of the acetone clusters can be calculated (see Figure 6). It turns out that in the region  $x_2 \approx .5$  more than 70 % of the

clusters are dissociated.

True cosolvency was verified for polystyrene-cyclohexane-acetone by measurements of the STAUDINGER - indices, additionally. Figure 5 presents data at 307.5 K. The  $x_2$  - dependence resembles that of the chemical potential. The  $[\eta]$  minimum at equimolar solvent mixture may be explained by enhanced specific interaction again.

In conclusion a noteworthy system has been discussed, where appropriate choice of the mixture of one dispersive and one specifically interacting solvent component allows to tailor made thermodynamic solution properties. The special role of acetone dissociation in mixtures with cyclohexane has been elucidated.

The question remains open how to transfer the findings on the LMWM acetone to macromolecules bearing corresponding specifically interacting groups. Probably, association is significantly diminished in polymeric chains, and the chance for enthalpic interaction with complementary groups in a second polymer may be enhanced because of the sterical situation. Work is in progress in order to transfer the knowledge derived from a specifically interacting LMWM to corresponding macromolecules.

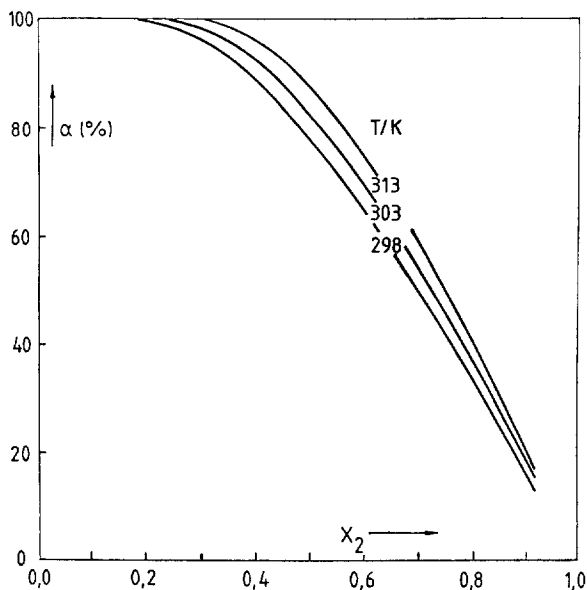


Figure 6. Dissociation of acetone in mixtures with cyclohexane

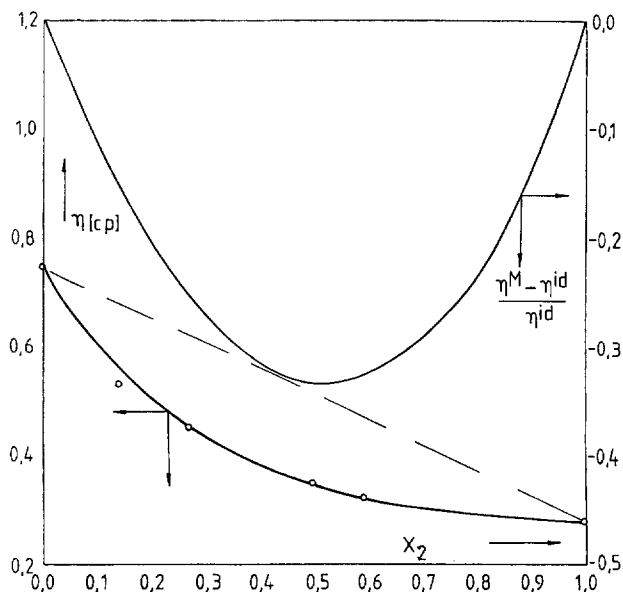


Figure 5. STAUDINGER indices of polystyrene - cyclohexane-acetone mixtures, 307.5 K

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