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Thermodynamics of Macromolecular Systems
3. Equilibrium Swelling Measurements Polystyrene-Cyclohexane-Acetone

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Summary

Equilibrium swelling measurements in the system polystyrene - cyclohexane - acetone within the temperature range from 288 to 323 K confirm the conclusion drawn from light scattering investigations (SCHUSTER, R. H., CANTOW, H.-J. and KLOTZ, S., 1982) that the system exhibits the characteristics of cosolvency. A thermodynamic analysis of the experimental data following the FLORY-HUGGINS-REHNER one-parameter equation in terms of χ, χ_H and χ_S is compared with that (CANTOW, H.-J. and SCHUSTER, R. H., 1982) based on the free energy two-parameter equation proposed by KONINGSVELD and KLEINTJENS. Thus, an unequivocal interpretation of the swelling thermodynamics of the ternary system could be reached, irrespective crosslink density of the network. The cosolvency effects are discussed in relation to the heat of mixing. The conclusion has been proved that the cosolvency is caused by breakdown of acetone clustering by dilution with cyclohexane.

Introduction

In the course of the investigation on specific interactions in macromolecular systems in the foregoing paper (SCHUSTER, R. H., CANTOW, H.-J. and KLOTZ, S., 1982) it has been pointed out that the thermodynamic solution properties of polystyrene in cyclohexane-acetone mixtures measured via light scattering show the characteristics of the cosolvency effect (WOLF, B. A. and MOLINARI, R. J., 1973). It was advanced for the explanation that the observed effect is caused by the special solvent structure generated, i. e. by breakdown of acetone clusters caused by dilution with cyclohexane. In the following the thermodynamic interactions in this system are studied at medium polymer concentrations by the isobaric swelling behaviour of polystyrene networks. Particularly it is tested wether an unequivocal description of such a ternary system, irrespective crosslink density, is possible, analogously like proved in the binary system polystyrene network-cyclohexane ((CANTOW, H.-J. and SCHUSTER, R. H., 1982).

Results and Discussion

The solubilization of a high molecular weight compound by two non-solvents, or by a weak solvent and a non-solvent, is a case of synergism being of scientific as well as of practical interest. Focussing on variation of temperature two groups may be distinguished:
A. The solvent power of the two pure liquids increases until at least one of them becomes a solvent.
B. The solvent power of the components never becomes high enough under isobaric conditions for complete miscibility.
The system polystyrene-cyclohexane-acetone belongs to group A.

The cosolvency effects are investigated by the procedure described in one of

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the foregoing papers (CANTOW, H.-J. and SCHUSTER, R. H.), with polystyrene networks exhibiting M_c's 3300, 4050, 5560, 7430, 11400, 14800, 36500, 165000 and 196000 in cyclohexane-acetone mixtures with the mole fraction of acetone x_2 = .000, .127, .268, .495, .685, .850 and 1.000 in the temperature range from 288 up to 323 K.

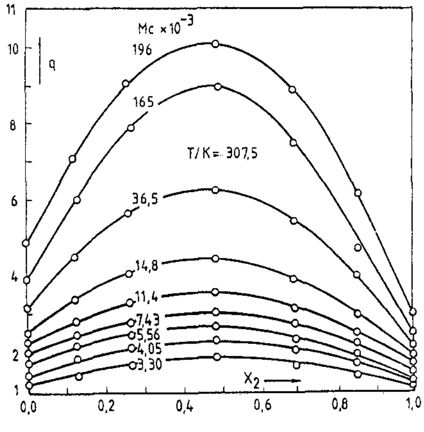

Figure 1. Degree of swelling of polystyrene network as function of x_2, with M_c as parameter, at 307.5 K

Some typical plots of the degree of swelling, q, versus solvent composition, x_2, are presented in Fig. 1. Independently of the degree of crosslinking, the equilibrium swelling shows up a typical extremum in the composition range $.45 < x_2 < .55$, which emphasizes a strong cosolvency effect.

In order to perform a thermodynamic analysis, at first the well known one-parameter free energy equation of FLORY and REHNER for equilibrium swelling of a network can be applied

$$\chi = [\ln(1-\phi_2) + \phi_2 + \frac{\bar{\rho}_2 \bar{v}_1}{M_c} (m^{-2/3}\phi_2^{1/3} - \frac{2\phi_2}{f})]\phi_2^{-2} \quad , \qquad (1)$$

with ϕ_2 the volume fraction of the network, $\bar{v}_1$ the partial molar volume of the solvent [$cm^3 mol^{-1}$], $\bar{\rho}_2$ the density of the polymer in the mixture, m the memory term and f the functionality of the crosslinks.

Because of the crosslinking copolymerization with m-DVB in bulk f=4 and m=1 was inserted for the calculation of χ.

The interaction parameters are functions of ϕ_2, T and x_2. The single liquid approximation (SCOTT, R. L., 1949) has been applied in order to reduce the number of independent variables. Threedimensional representations of the interaction parameter as function of ϕ_2 and T are presented in Figure 2, with the solvent composition indicated. The trends of the thermodynamical behaviour in the investigated system are evident. Firstly, the χ-values at given ϕ_2 and T are functions of x_2. They diminish with increasing acetone concentration, pass through a minimum around x_2 = .50 and rise to high values, according to the precipitant character of associated acetone. These findings extend the light scattering results from the foregoing paper to volume fractions up to .7.

The best solution quality from the thermodynamic standpoint is attained, when the solvent structure becomes critical in a way. It has been argued (WOLF, B. A., 1978) that the assumption of a certain "incompatibility" between both the solvent components suffices to explain the cosolvency phenomenon. For the present system this interpretation as well as attempts of explanations given in terms of cohesive energy densities have shortcomings. Indications are given from the measurements of excess volumina and viscosities of pure cyclohexane-acetone mixtures (CANTOW, H.-J. and SCHUSTER, R. H., 1982) that the breakdown of acetone clusters by dilution with cyclohexane may be the major contributor of the observed effect.

From Fig. 2 it is evident that the synergistic solution properties of the mixed solvent are reflected also in the ϕ_2-dependence of χ. The minimum dependence is observed in the thermodynamically most favourable solvent mixture. At constant x_2 the ϕ_2 dependence of the interaction parameter is more pronounced, generally, at lower temperatures. No synergism is observed concerning the temperature dependence of χ, which decreases continuously with the acetone concentration.

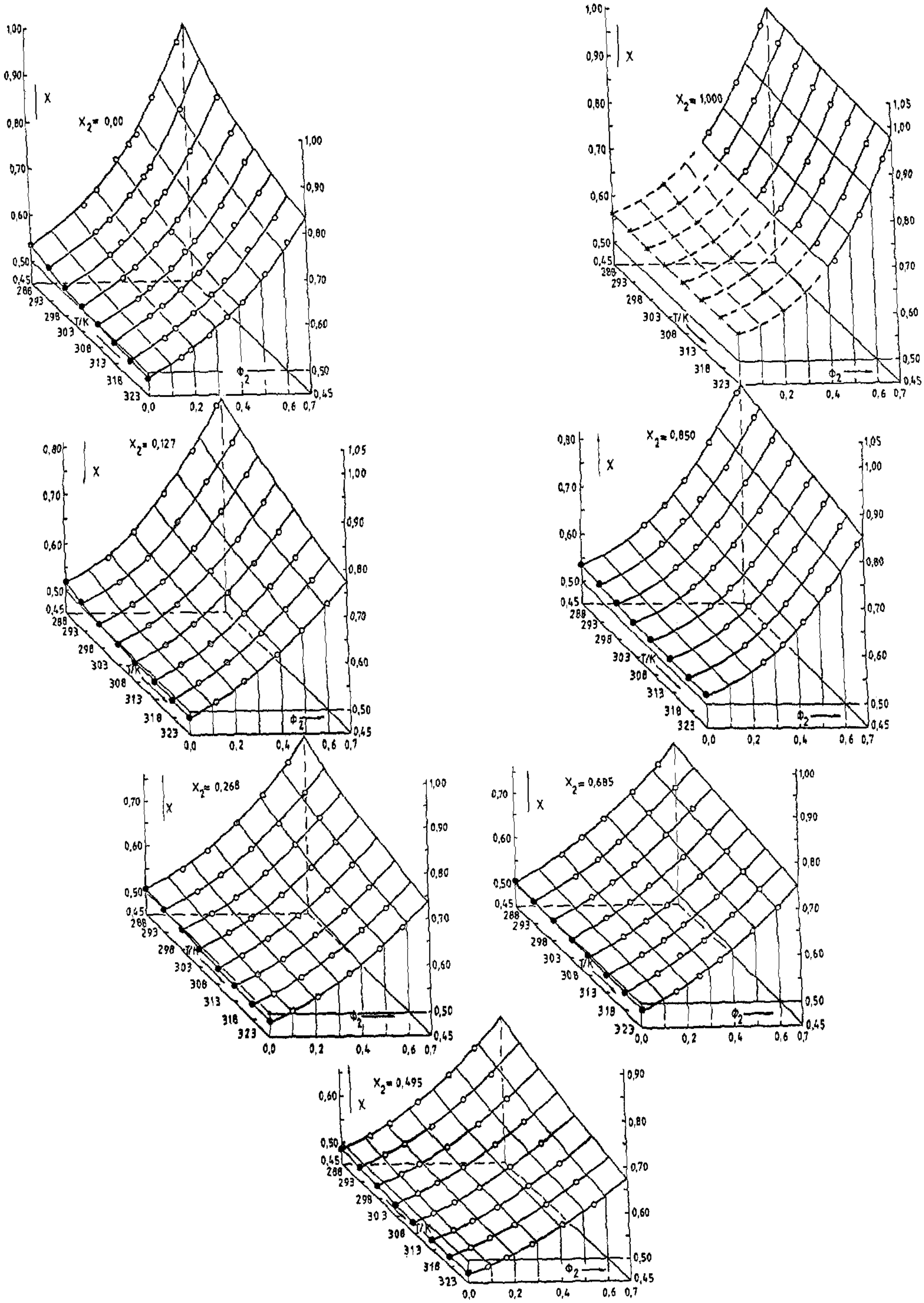

Figure 2. χ as function of Φ_2, T and x_2 for polystyrene - cyclohexane - acetone

The surfaces presented in Figure 2 can be expressed by an empirical function

$$\chi(x_2) = a_1 + (a_2 + a_3 T) + (a_4 + a_5 \phi_2)\phi_2 + (a_6 + a_7 T + a_8 \phi_2 + a_9 \phi_2 T)\phi_2 T$$

The coefficients are given in Table I. (2)

Table I. Coefficients of Equation 2, polystyrene network-cyclohexane-acetone

x_2	a_1	$a_2 x 10^2$	$a_3 x 10^4$	a_4	a_5	$a_6 x 10^2$	$a_7 x 10^4$	$a_8 x 10^1$	$a_9 x 10^4$
.000	3.203	-1.647	.250	-7.351	34.83	4.869	-.780	-2.189	3.478
.127	2.261	-1.068	.1605	-2.979	13.41	1.886	-.274	- .7703	1.121
.268	2.827	-1.449	.2236	-5.812	17.32	3.904	-.6317	-1.071	1.679
.495	1.922	- .903	.1402	-2.842	11.02	1.984	-.3224	- .669	1.028
.685	1.458	- .5777	.0854	- .9244	5.171	.7656	-.1256	- .3023	.4601
.850	1.967	- .8958	.1383	-1.151	6.616	.8184	-.1279	- .3730	.5662
1.000	.8598	- .1733	.0252	-1.828	- .6727	1.182	-.1864	.1065	- .1779

It can be seen easily that the thermodynamic description of the system polystyrene network - cyclohexane - acetone, even in the single liquid approximation, runs somewhat into difficulties, in as much as the physical meaning of the coefficients is vague. Similar observations concerning polynomial expansions of χ have been made recently for polystyrene networks swollen in cyclohexane (BORCHARD, W., 1982, and CANTOW, H.-J. and SCHUSTER, R. H., 1982).

A consequent split of the interaction parameter into an enthalpic and an entropic term leads from Equ. (2) to the empirical expressions

$$(\chi_H)_{x_2} = T(\partial\chi/\partial T)_{p,\phi_2,x_2} = -T[(a_2 + 2a_3 T) + (a_6 + a_8 \phi_2)\phi_2 + 2(a_7 + a_9 \phi_2)\phi_2 T] \qquad (3)$$

$$(\chi_S)_{x_2} = (\partial(T\chi)/\partial T)_{p,\phi_2,x_2} = (a_1 + a_4 \phi_2 + a_5 \phi_2^2) + 2(a_2 + a_6 \phi_2 + a_8 \phi_2^2)T + 3(a_3 + a_7 \phi_2 + a_9 \phi_2^2)_{\text{,}} T^2 \qquad (4)$$

The calculated χ_H- and χ_S -surfaces for x_2 = .000, .495 and 1.000 are presented in Figure 3. No synergistic effect is observed for χ_S versus the acetone concentration. There are generally more positive χ_S values at higher x_2. In the same way the temperature dependence of χ_S at constant ϕ_2 is more pronounced at lower acetone concentrations. Focussing at the ϕ_2-dependence of the χ_S isotherms, the most interesting fact seems to be the switch of the surface from negative towards positive χ_S values at high x_2.

For the χ_H surface it turns out that the T-dependence of χ_H at constant ϕ_2 becomes smaller at higher x_2-values. Interesting to note the tendency of the ϕ_2-dependence of the χ_H isotherms. They run towards smaller values with growing x_2. It is evident, however, that they never switch to the negative side.

It is worthwile to analyze the complementary effect of the χ_H and χ_S surfaces. In cyclohexane, at low temperatures, large positive χ_H values are counteracted by large negative χ_S values, whereas at higher temperatures low positive χ_H's are added to low positive χ_S's. The tendency towards phase separation causes an increasing number of interactions between chain segments. For the mixture with the pronounced cosolvency effect the situation is complex: Positive χ_S (approximately for the entire surface within the range .2 - .45) are added to lower χ_H (around .0 - .4). In the non-solvent acetone an approximately "athermic" χ_H - (.08 - .2) and a pronounced positive χ_S -surface exists. These results make conspicuous that the thermodynamic solution qualities of the solvent mixture are governed in an accentuated mode by the entropic contribution to χ.

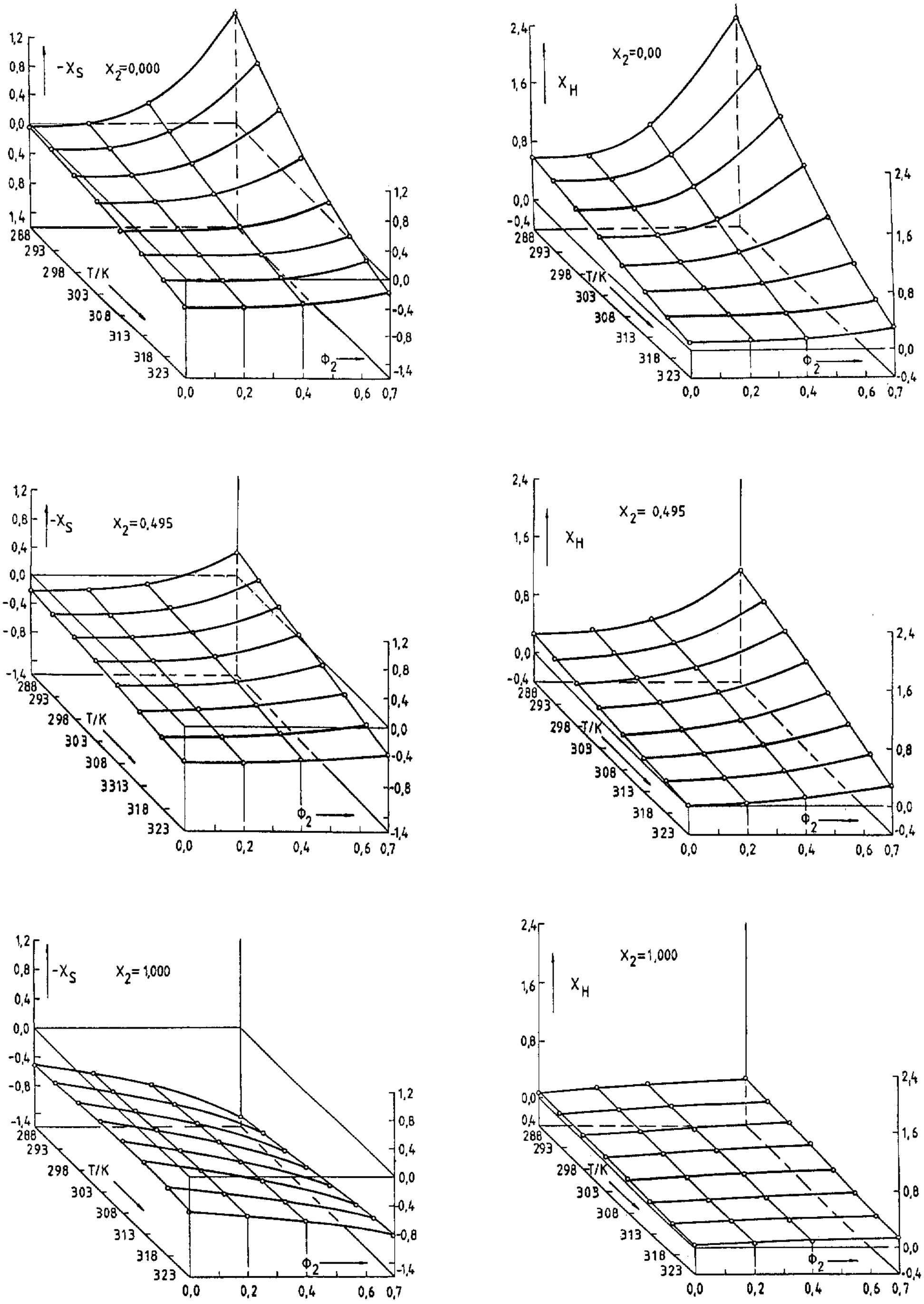

Figure 3. χ_S and χ_H as function of ϕ_2, T and x_2, polystyrene - cyclohexane - acetone

Recently we have reported (CANTOW, H.-J. CANTOW and SCHUSTER, R. H., 1982) that applying the two-parameter KONINGSVELD-KLEINTJENS equation for polymer solutions (1971) to gels an unequivocal interpretation of swelling thermodynamics for the binary system - polystyrene network - cyclohexane - could be reached, irrespective crosslink density of the networks. In the following it is demonstrated that this approach enables a thoroughgoing thermodynamic analysis of the ternary system under investigation too. On the basis of the equilibrium swelling condition

$$(\partial\Delta G^{M}/\partial n_1)_{p,T} = (\partial\Delta G^{el}/\partial n_1)_{p,T} \qquad (5)$$

an expression for the chemical potential of the solvent in a swollen gel follows with

$$(\partial\Delta G^{M}/\partial n_1)_{p,T} = RT[\ln 1 - \phi_2) + 1 - \frac{1}{X})\phi_2 + (\alpha_o + \frac{\beta_o(1-\gamma)}{(1-\gamma\phi_2)^2})\phi_2{}^2] \qquad (6)$$

$$\alpha_o + \frac{\beta_o(1-\gamma)}{(1-\gamma\phi_2)^2} = \phi_2{}^2[\ln(1-\phi_2] + \phi_2 + \frac{\rho_2\bar{v}_1}{M_c}(\phi_2{}^{1/3} - \frac{2\phi_2}{f})] \qquad (7)$$

$$\chi = \alpha_o + \beta_o(1-\gamma)/(1-\gamma\phi_2)^2 \quad . \qquad (8)$$

α_o is the excess entropy parameter, β_o the interaction enthalpy parameter, $\gamma = 2/z$ the coordination number of the lattice and X the degree of polymerization of the dissolved polymer.

For the ternary swelling system under investigation it has been assumed that z does not change with x_2 and T. z = 8.4 was choosen, as derived for polystyrene - cyclohexane at Θ-conditions (SCHOLTE, T. G., 1971). This simplification implies some uncertainty with respect to α_o and β_o. It appears to be unrealistic to eliminate the cosolvency effect arising at medium x_2 by a coordination number z< 2.5. Consequently, constancy of z has been maintained, because the effective trend with x_2 would not influence the conclusions critically. Figure 4 demonstrates that the two-parameter approach is succesfully applicable for the three-component system studied. Excess entropy α_o and the enthalpy parameter β_o are plotted versus T and x_2.

α_o shows up negative values indicating relatively ordered states on the limits of the binary mixture. In the center of the x_2-interval the excess entropy develops towards low negative values, which indicate that the mixture with maximal cosolvency has a global entropy nearest the combinatorial one.

The β_o -parameter surface shows a characteristic deep exothermic valley at $x_2 \simeq .5$. The solvent effect, expressed as $d\beta_o/dx_2$ and $d\alpha_o/dx_2$, is in the module higher towards pure acetone than towards cyclohexane. It is evident that non-associated acetone contributes more to the cosolvency than the weak solvent cyclohexane. The ambivalent nature of acetone -

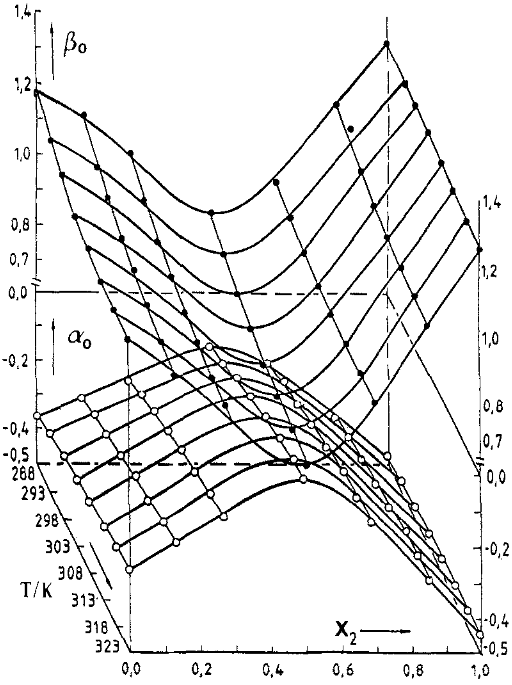

Figure 4. β_o and α_o versus x and T for polystyrene network - cyclohexane - acetone

non-solvent when associated, and relatively good solvent as free molecule - shows up clearly.

The hypothesis that the structure of the solvent mixture is determining the cosolvency effect through breakdown of acetone clusters by dilution with an inert solvent is consolidated further by measurements of the heat of mixing of the solvent components. The excess heat of mixing of cyclohexane with acetone (Figure 5) exhibits an endothermic maximum of 1.65 kJmol $^{-1}$ at $x_2 \simeq .5$. It coincides with the maximum cosolvency composition. The positive excess volumina as well as the viscosity of the solvent mixture being lower than the ideal one (SCHUSTER, R. H., CANTOW, H.-J. and KLOTZ, S., 1982) support the conclusion: Because of the breakdown of the acetone clusters by dilution the free energy of the pure solvent mixture rises, and in parallel the solvatation power of the mixture is enhanced. Even when the action of a certain "incompatibility" of the components (WOLF, B. A., 1978) may assist the effect, non-associated acetone molecules exhibiting high "activity" dominate the solution qualities of mixtures around $x_2 = .5$.

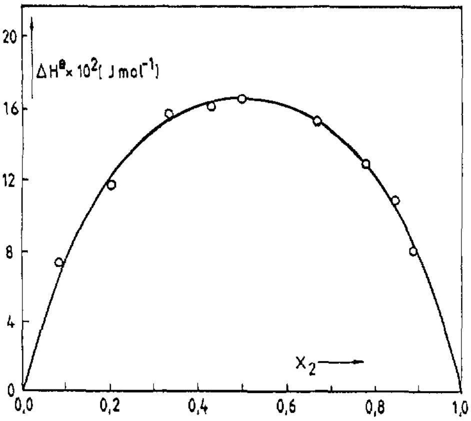

Figure 5. Excess heat of mixing of cyhexane - acetone

In conclusion, an unequivocal interpretation of the swelling behaviour of a ternary system could be reached by applying the two-parameter KONINGSVELD-KLEINTJENS equation. It has been proven that this approach not only cancels the concentration effect in solutions of linear macromolecules. It can be applied successfuly to swollen binary (CANTOW, H.-J. and SCHUSTER, R. H., 1982) and ternary systems also, where the topology of the networks induces conformational effects additionally. Light scattering measurements have yielded the respective information for infinite dilution. Work is in progress to study the thermodynamical data of pure polystyrene by inverse gas chromatography investigations. Hopefully these studies will contribute to build up a basis for understanding problems of polymer compatibility by the concept to substitute macromolecular components by representative low molecular weight models.

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References

BORCHARD, W., 6th Eurpean Network Group Meeting, Strasbourg (1982)

CANTOW, H.-J. and SCHUSTER, R. H., Polymer Bulletin **8**, 225 (1982)

FLORY, P. J., Principles of Polymer Chemistry, Cornell Univ. Press, Ithaca (1953)

KONINGSVELD, R. and KLEINTJENS, L. A., Macromolecules **4**, 637 (1971)

SCHOLTE, T. G., J. Pol. Sci. A-2, **9**, 1553 (1971)

SCHUSTER, R. H., CANTOW, H.-J. and KLOTZ, S., Polymer Bulletin **8**, 351 (1982)

SCOTT, R. L., J. Chem. Phys. **17**, 268 (1949)

WOLF, B. A. and MOLINARI, R. J., Makromol. Chem. **173**, 241 (1973)

WOLF, B. A., Makromol. Chem. **179**, 2265 (1978)

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