Thermodynamic Solution Properties of Three Polymers Exhibiting Lower Critical Solution Temperature

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The second virial coefficients of cellulose-, amylose- and polyvinyl-carbanilates in several solvents were measured as a function of the temperature. In three cases theta temperatures and phase separations were observed on heating the solutions. The second virial coefficients were divided into two parts A_{2S} *and* A_{2H} *which correspond to entropy and heat of dilution. In a plot of* A_{2S} *against* A_{2H} *curves were obtained, which sometimes reverse their direction with increasing temperature. The results are discussed on the basis of theories of Prigogine and of Patterson, and are not reasonably explained by the concept of dispersion forces.*

Die zweiten Virialkoeffizienten von Cellulose-, Amylose- und Polyvinylcarbanilaten in verschiedenen Lösungsmitteln wurden in Abhängigkeit von der Temperatur gemessen. In drei Fällen wurden Theta-Temperaturen und Phasentrennungen beim Erwärmen der Lösungen beobachtet. Die Virialkoeffizienten wurden in zwei Anteile, A_{2S} *und* A_{2H} *zerlegt, die den Verdünnungsentropien und den Verdünnungswarmen zugeordnet sind. Bei einer Auftragung von* A_{2S} *gegen* A_{2H} *werden Kurven erhalten, deren Durchlaufungsrichtung sich mit steigender Temperatur manchmal umkehrt. Die Ergebnisse werden an Hand der Theorien von Prigogine und von Patterson diskutiert, und es wird gezeigt, daß sie mit dem Konzept von Dispersionskräften nicht erklärt werden können.*

IN SOLUTIONS of high polymers separation into two liquid phases normally appears if the temperature is decreased below a critical value. This critical temperature is called the upper critical solution temperature (UCST) as it lies at the top of the two-phase region in the temperature versus composition phase diagram. Up to 1959 only a few systems with lower critical solution temperatures (LCST) were found, which show phase separation on heating the solution. Well known examples are the aqueous solution of polyvinylmethylether[1], partly substituted methylcellulose[2, 3], and polyvinylalcohol with some residual acetate groups[4, 5]. For the latter, Rehage recently found a closed loop of mixing with both upper and lower critical solution temperatures[5]. The behaviour of these systems is atypical but not really surprising, as water is a liquid with very unusual properties. The phase separation may well be caused by so-called hydrophobic interaction, which is a peculiarity of the structure of water.

In 1959, however, Freeman and Rowlinson[6] first observed phase separation on heating solutions of non-polar polymer systems[7–14]. The belated discovery of this phenomenon is due to the fact that this type of phase separation takes place at temperatures far above the boiling point of the solvent. Thus higher pressures are needed for detecting this kind of separation. Very

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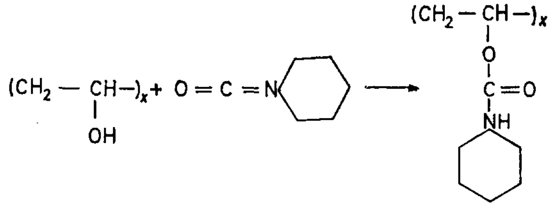
recently this behaviour was satisfactorily interpreted by the theories of Prigogine and Patterson[15–17].

The present paper gives a report on three other non water-soluble systems, which also show phase separation on heating. These systems differ from those mentioned earlier by the fact that phase separation appears at atmospheric pressure and at temperatures well below the boiling points of the solvents.

The polymers concerned are the carbanilates of cellulose, amylose, and polyvinylalcohol. These derivatives are easily prepared by treating the polymers with phenylisocyanate in hot pyridine[18, 19]. In the case of polyvinylalcohol the reaction is as follows:



Polysaccharides similarly acquire three carbanilate groups per monomer unit.

It is of special interest to compare the solutions and the thermodynamic properties of these three types of polymer chains, because the two polysaccharides are typical rigid chains, whereas polyvinylcarbanilate is more flexible[20, 21].

In the first stage we were interested in the properties of dilute solutions, hence the second virial coefficient and its temperature dependence was measured by means of light scattering in the range 2° to 95°C.

TEMPERATURE DEPENDENCE OF THE SECOND VIRIAL COEFFICIENT A_2

In *Figures 1* to *3* the second virial coefficients are plotted against the temperature for a variety of solvents. In amylose tricarbanilate (AC) and cellulose tricarbanilate (CC) A_2 decreases sharply with increasing temperature in most of the solvents. AC in diethyleneglycol–diethylether exhibits a theta temperature ($A_2=0$) at 90°C, and separation occurs a few degrees above. Similarly theta temperatures were found for CC in both diethyleneglycol–dibutylether and dibutylketone at 45°C. In all these cases the solvents are long chains.

In contrast the behaviour of AC in pyridine is similar to other systems exhibiting the upper critical solution phenomenon, but recently we noticed that this behaviour is caused by an ageing effect. If a freshly prepared AC is used, or if the polymer is reprecipitated from a dioxan solution in water, AC shows similar properties to CC in pyridine. We presume that AC may form a stabilized helix when stored for more than a year.

The second virial coefficient for polyvinylcarbanilate (PVCarb) also decreases slightly with temperature in most solvents used. But the decrease

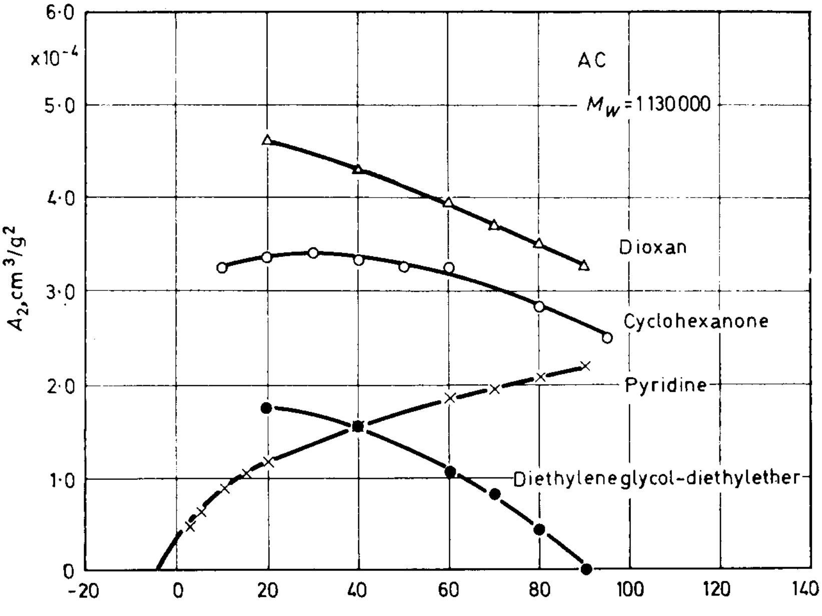


Figure 1

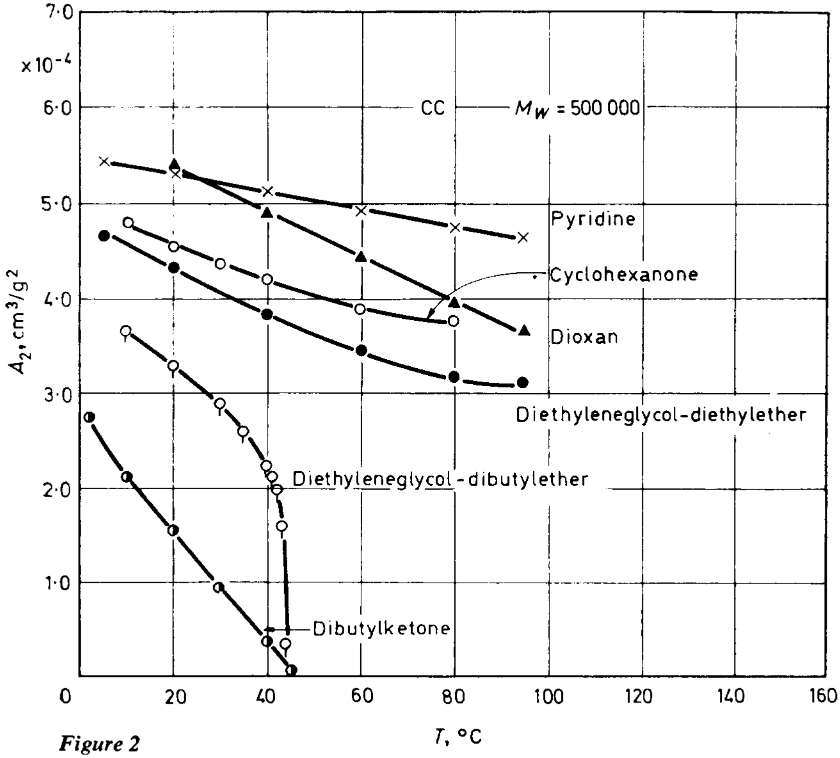


Figure 2

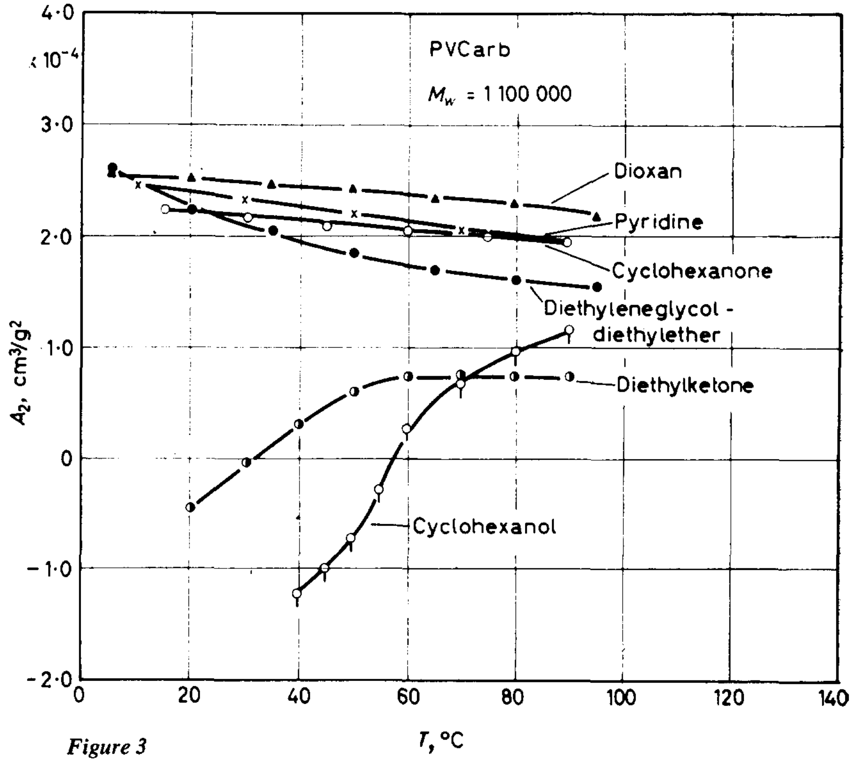


Figure 3

Figures 1–3—Dependence of the second virial coefficient on temperature for amylosetricarbanilate (AC), for cellulosetricarbanilate (CC), and for polyvinylcarbanilate (PVCarb) in several solvents

is rather less pronounced, and up to now no solvent with a theta point on heating could be found. (We presume that diethyleneglycol–dipropylether may behave in a similar manner, but unfortunately this solvent is not available.) On the other hand two Flory theta points were obtained for PVCarb, i.e. in diethylketone at 35°C and in cyclohexanol at 55°C. Recently cyclohexanol was shown[22] to be a Flory theta solvent for CC at about 80°C, and also for AC this solvent exhibits a Flory theta point as phase separation occurs below 120°C. Phase separation for CC appears also in methylglycol–ether below 40°C. But the true theta temperature could not be determined as association takes place before reaching the value $A_2=0$.

HEAT AND ENTROPY OF DILUTION

From the temperature dependence of A_2 one can calculate the heat and the entropy of dilution. These calculations are based on the well-known relationship between the osmotic pressure and the chemical potential difference

$$\pi V_1 = -\Delta\mu_1 = -(\Delta\mu_1^i + \Delta\mu_1^e) \tag{1}$$

where V_1 is the partial specific volume of the solvent and the superscripts indicate the ideal and the excess chemical potential respectively. For very dilute solutions the excess chemical potential is related only to the second virial coefficient

$$RTA_2 \simeq -\Delta\mu_1/C^2V_1$$

According to the rules of thermodynamics $\Delta\mu_1^e$ may be divided into two parts corresponding to the heat and to the excess entropy of dilution. Using this relationship two parts of A_2, i.e. A_{2S} and A_{2H}, may be defined as

$$RTA_2 = T(\Delta s_1^e - \Delta h_1)/V_1C^2 \equiv RT(A_{2S} + A_{2H}) \tag{3}$$

As Δs_1^e and Δh_1 can be calculated from the temperature dependence of $\Delta\mu_1^e$ the same is possible for A_{2S} and A_{2H} from A_2. Thus the following equations of evaluation can be derived[23]

$$\begin{aligned} A_{2S} &= T\partial A_2/\partial T + A_2(1-\alpha T) \\ A_{2H} &= A_2 - A_{2S} \end{aligned} \tag{4}$$

where the thermal expansion α is taken into account.

THETA CONDITIONS

In most cases A_2 decreases as the temperature is lowered. Then as shown by equation (4) A_{2S} is always positive, whereas A_{2H} is negative if A_2 is not too large. Positive values of A_{2S} indicate positive excess entropies of dilution whereas negative A_{2H} values indicate positive values of the heat of dilution—as by definition A_{2H} is proportional to $-\Delta h_1$. Thus these solutions are endothermic. Under theta conditions A_2 equals zero and consequently $A_{2S} = -A_{2H}$. This relationship is valid for theta points obtained on heating the solution as well as for Flory theta points but the excess entropy of dilution becomes negative and A_{2H} positive when the theta points are obtained on heating. The solutions therefore are strongly exothermic in the vicinity of these types of theta temperatures, whereas they are highly endothermic at Flory theta points.

RELATIONSHIP BETWEEN A_{2S} AND A_{2H}

A_2 was divided into parts of A_{2S} and A_{2H} according to equation (4) for each series of measurements in the above mentioned solvents. G. V. Schultz and co-workers plotted A_{2S} against A_{2H} for PMMA as measured in several solvents at room temperature, and they found a relationship nearly independent of the solvents used[23, 24]. Such behaviour could not be observed in the present measurements on the carbanilates. This is shown in *Figures 4* to *6*. In the cases of AC and PVCarb the experimental points lie near the dotted diagonal in the figures. Any possible theta points must lie on these diagonals. The arrows show the direction of increasing temperature. From the measurements of AC in cyclohexanone one can see that the

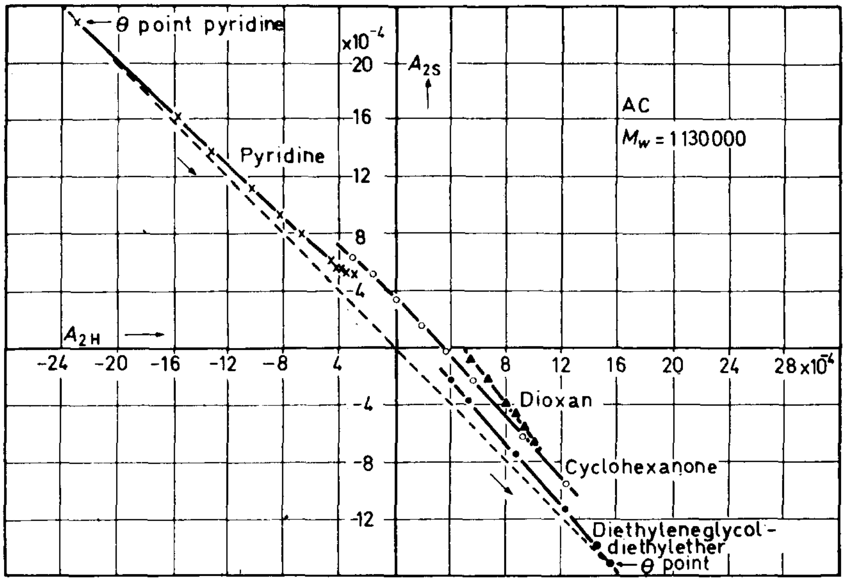


Figure 4

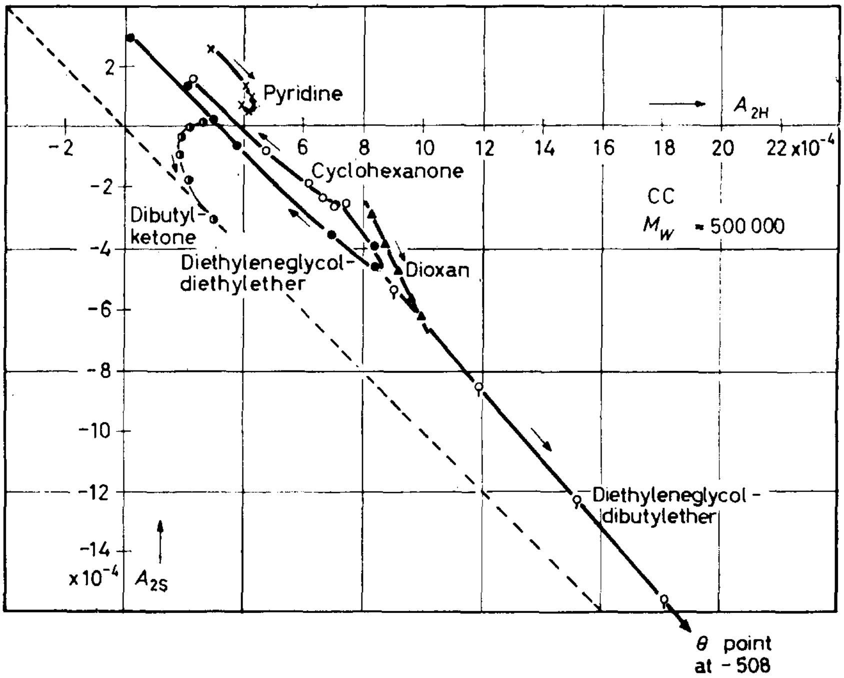


Figure 5

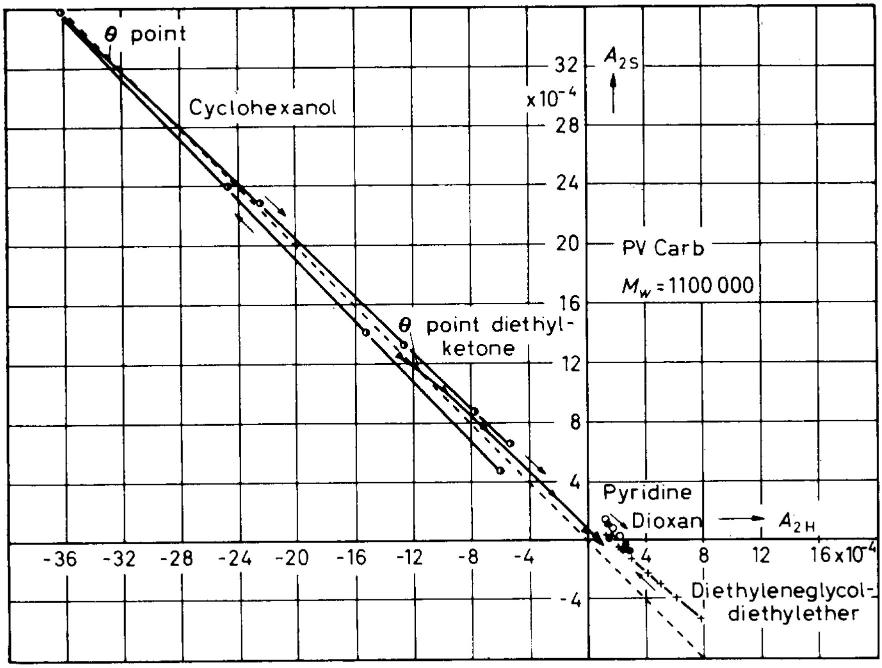


Figure 6

Figures 4–6—Relationships between A_{2S} and A_{2H} determined from measurements of A for AC, CC and for PVCarb. Arrows show directions of increasing temperature

solution, endothermic at room temperature, becomes more and more exothermic at higher temperatures. Hence there is a high probability for the existence of two theta points in the same solvent.

From the measurements of PVCarb in cyclohexanol the direction of the curve is reversed as the temperature passes through the theta temperature. This reversal is much sharper for the solutions of CC. Up to now this strange behaviour has not been observed for other systems.

DISCUSSION

Although measurements have been performed only in the dilute range some conclusions can be drawn concerning the interaction forces between the carbanilate molecules in solution. The striking feature of these solutions is the appearance of LCSTs. It can be seen immediately that these new examples cannot belong to the Prigogine–Patterson type for two reasons: (*i*) According to the theories of Prigogine and of Patterson the phase separation should occur in the vicinity of the critical liquid–vapour point of the solvent whereas in the carbanilates it takes place at temperatures below the boiling point of the liquid; (*ii*) With increasing length of the solvent molecules the LCST should be shifted to higher temperatures. This was clearly shown by the experiments of Delmas and Patterson on polyisobutylene in alkanes of different lengths[10]. In contradistinction to that the LCST for the carbanilate solutions is shifted to lower temperatures.

On the other hand the new examples cannot belong to the types of aqueous solutions mentioned in the introduction. Water has a strange structure the order of which becomes higher if a solute with some hydrophobic sections is added ('iceberg' formation). The phase separation on heating is presumably caused by this ordering effect of the water structure. The organic solvents used in this investigation, however, do not exhibit ordered structures similar to that of water. Thus other reasons must be responsible for the LCST observed in the carbanilate systems. The polycarbanilates possess very polar groups which are expected to induce orientation of the likewise polar solvent molecules. This orientation, which is quite dissimilar to the order in water caused by the hydrophobic interaction is connected with negative excess entropies of dilution as observed in many other polar systems. The development of theories involving orientation has had little success for polymer solutions[27], but for low molecular weight components Barker was able to calculate three models on the basis of the lattice theory[28]. Two of these exhibit UCSTs and involve some peculiarities. The third model yields a closed coexistence curve with LCST and UCST. In this model one polar group of the one component induces a high polarization effect and thus a strong interaction on the other component. Barker believes that the system glycerol–toluidine is appropriately described by this model. As the carbanilates are also derivatives of aniline this model may possibly be appropriate for these solutions, too. But the carbanilates are more complicated than toluidine because there is a facility for H-bonding between CO and NH groups of different substituents, and these H-bonds will have a strong orientation effect and will drastically influence the solution properties.

The author thanks Professor M. Gordon for his comments on the manuscript and Miss G. Becker for her assistance in performing the light scattering measurements. He is also indebted to the Deutsche Forschungsgemeinschaft for financial support.

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(*Received September 1968*)

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