

Critical Solution Temperatures in Cellulose Diacetate-Acetone Solutions

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Thermodynamic properties of acetone solutions of cellulose diacetate (a degree of substitution, DS = 2.46) were examined by means of solution stability experiments over the wide range of temperature. The solutions were separated into two-phase at elevated temperatures of around 170°C, the lower critical solution temperature having been determined. On the other hand, no phase separation was observed at low temperatures. The latter observation is not in accord with a published result on similar materials. A theoretical consideration is given to substantiate the observed phenomenon.

1. INTRODUCTION

Phase separation in a polymer-solvent system occurs on cooling when the system is endothermic. The temperature at which a dilute solution of an infinite molecular-weight polymer separates into two liquid phases is known as the Θ point. Historically, the Θ point has always been associated with an upper critical solution temperature (UCST), which lies, for monodisperse polymer, at the top of a two-phase region. On the contrary, if a polymer-solvent system is exothermic, phase separation will occur on heating to what is known as the lower critical solution temperature (LCST) since it lies at the bottom of a two-phase region. Accordingly, there exists another Θ point associated with LCST.

Heretofore we simply distinguished polymer-solvent systems according to whether they were endothermic or exothermic. Such a point of view is not necessarily valid when the wide range of temperature is concerned. In general, thermodynamic properties of polymer solutions are temperature-dependent, and hence the endothermic behavior at room temperature may alter to the exothermic at elevated temperatures. Since the work of Freeman and Rowlinson,¹⁾ a number of

polymer-solvent pairs have now been identified which show both a UCST and an LCST within an experimentally accessible range.²⁻⁷⁾ The LCST usually lies far above the boiling point, but surely below the critical point of the solvent. This has been recognized as a completely general phenomenon for high polymer solutions. In addition, it has been disclosed that phase separation at LCST is owing to the difference in thermal expansion between solvent and solute.

The system cellulose acetate-acetone is one of the polymer-solvent pairs which have extensively been studied.³⁾ Both the UCST and LCST occurs for the triacetate. Although it is the case with the diacetate of low molecular weight, the UCST and LCST coalesce for high molecular weight samples of the diacetate. In other words, the diacetate becomes insoluble, when the number-average molecular weight exceeds, according to Cowie et al.,³⁾ about 10^5 .

In the preceding papers,⁸⁻¹⁰⁾ thermodynamic and conformational study on cellulose diacetate in acetone have been carried out. According to the results obtained, a fraction of the diacetate is still soluble in acetone even though the number-average molecular weight of the sample is about twofold the limit Cowie et al. stated.³⁾ The Flory entropy and enthalpy parameters, ϕ_1 and κ_1 , take the values of -0.010_8 and -0.05_1 , respectively, at 25.5°C [Ref. 10]. This implies that (i) the solvent nature of acetone is configurationally poor, but

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thermally good, (ii) the present system is exothermic, and (iii) there exists some specific interaction between cellulose diacetate and acetone. These results are not necessarily in accord with those of Cowie et al.³⁾ in some respects. Since better understanding is expected to attain from an examination of the solution stability over the wide range of temperature, the UCST and LCST measurements were carried out. This paper describes some preliminary results of such an experiment and discusses thermodynamic properties of the system cellulose diacetate-acetone.

2. EXPERIMENTAL

2.1 Materials

The sample used is an unfractionated cellulose diacetate. The sample preparation has been described in detail elsewhere.⁸⁾ The combined acetic acid content is 55.6 wt% (a degree of substitution, DS = 2.46) and the weight- and the number-average molecular weights as determined by gel permeation chromatography are $M_w = 12.0 \times 10^4$ and $M_n = 5.5 \times 10^4$, respectively. The solvent acetone (Nakarai Chemicals, guaranteed grade) was distilled and kept over molecular sieves 4A. In order to suppress the thermal degradation of the diacetate, the stabilizer, 2,6-di-*tert*-butyl-*p*-cresol was added to the solvent at 1 wt% concentration.

2.2 Cloud-point measurements

Several solutions of the unfractionated diacetate in acetone were prepared in the concentration range 1–11.5 wt% in test tubes (inner diameter = 10 mm). After the air in a tube was replaced with dry nitrogen, the tube was flame sealed. A glass ball was inserted in each tube for effective stirring of the solution.

For the LCST measurements, the solution tubes were slowly warmed (ca. 1°C/10 min) while stirring in an electric thermostat of the air bath type, which was designed especially for LCST measurements.¹¹⁾ The main body of this apparatus is made of a copper block (diameter \times height = 15 cm \times 40 cm) with a hole at the center, in which the tube and its case can be situated. The copper block was heated by means of four thermocoax heater (Phillips) imbedded therein. Cloud point was recorded as the temperature at which the solution became heavily turbid. The UCST measurements were tried by using a carbon dioxide-methanol

bath over the temperature $> -78^\circ\text{C}$ and liquid nitrogen at its boiling point.

3. RESULTS AND DISCUSSION

In Fig. 1, the observed cloud points at elevated temperatures are plotted against the weight fraction w_2 of cellulose diacetate. The LCST is estimated to be 165.3°C from the bottom of this cloud-point curve. Since the polydispersity displaces the critical point from the bottom to some point on the right branch of the curve, this temperature should be called, more correctly, the precipitation threshold.¹²⁾ Here we use the term LCST in such an approximation that the polydispersity effects are neglected. An appearance of LCST had been expected, for the present system was proved to be exothermic.¹⁰⁾ This result coincides with those of Cowie et al.³⁾ and of Bolotnikova et al.¹³⁾

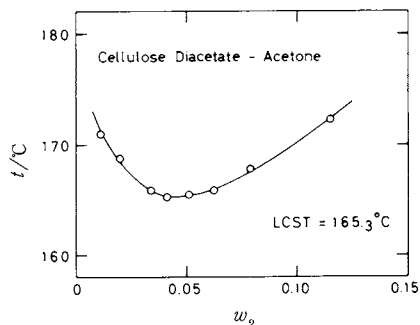


Fig. 1. Cloud-point curve for acetone solutions of unfractionated cellulose diacetate (DS = 2.46).

As for UCST measurements, no cloud points were observed at the carbon dioxide-methanol temperatures. No phase separation occurred even when tubes containing solutions were immersed into liquid nitrogen. Naturally, the solutions were frozen white, but when redissolved, they became transparent solutions again. This observation conflicts with that reported by Cowie et al.³⁾ The cloud points they observed exist around 0°C for a sample (DS = 2.8, $M_n = 95000$) and around -30°C for another (DS = 2.2, $M_n = 68700$). In spite of the fact that the DS value of our acetate is just between those of their two samples, acetone solutions of our diacetate were thermally stable. As has been discussed,¹⁰⁾ the exothermic nature of the system is due to the solvation of acetone molecules onto the polymer by hydrogen bonding. Since

the hydrogen bond is stable at lower temperatures, it seems to be legitimate that on cooling phase separation does not occur. This fact can be substantiated by a theoretical consideration.

In the classical Flory theory of polymer solutions,¹⁴⁾ the reduced excess chemical potential at infinite dilution, $-B$, is separated into its enthalpic (κ_1) and entropic (ϕ_1) contributions, so that

$$B = \lim_{\phi_2 \rightarrow 0} \left(-\frac{(\mu_1 - \mu_1^0)^E}{RT\phi_2^2} \right) \\ = \lim_{\phi_2 \rightarrow 0} \left(\frac{\bar{S}_1^E}{R\phi_2^2} - \frac{\bar{H}_1^E}{RT\phi_2^2} \right) = \phi_1 - \kappa_1 \quad (1)$$

where ϕ_2 is the volume fraction of the polymer and the other symbols have usual significance. From this definition one obtains the following relations

$$(\partial TB/\partial T)_p = \phi_1 \quad (2a)$$

$$(\partial B/\partial T)_p = \kappa_1/T \quad (2b)$$

We also define another quantity ξ_1 by the relations

$$\xi_1 = T(\partial\phi_1/\partial T)_p \quad (3a)$$

$$= (\partial T\kappa_1/\partial T)_p \quad (3b)$$

Here, ξ_1 denotes the value of the reduced excess partial molar heat capacity of dilution at constant pressure and infinite dilution. Eichinger integrated eqs. (3a) and (3b) along an isobar with use of a Taylor series about Θ_u , i.e., the Θ point associated with UCST.¹⁵⁾ We integrate them about the Θ point associated with LCST, Θ_L , instead. In the same approximation as afforded by Eichinger, one obtains the following truncated expressions for ϕ_1 , κ_1 , and $B(T)$.

$$\phi_1 = \phi_{1,L} - \bar{\xi}_1 \ln(\Theta_L/T) \quad (4a)$$

$$\kappa_1 = \phi_{1,L}(\Theta_L/T) + \bar{\xi}_1(1 - \Theta_L/T) \quad (4b)$$

$$B(T) = \phi_{1,L} \left(1 - \frac{\Theta_L}{T}\right) - \bar{\xi}_1 \left[\ln\left(\frac{\Theta_L}{T}\right) + \left(1 - \frac{\Theta_L}{T}\right) \right] \quad (4c)$$

Here, for simplicity, ξ_1 has been assigned an average value $\bar{\xi}_1$ in the temperature interval between Θ_U and Θ_L . Since the values of ϕ_1 and κ_1 have experimentally been determined,¹⁰⁾ this quantity can be expressed as

$$\bar{\xi}_1 = 5.74\phi_{1,L} + 0.73$$

when Θ_L is set to be 160°C.

On the other hand, the second virial coefficient,

A_2 , can be written with use of ϕ_1 and κ_1 as follows:

$$A_2 = (\bar{v}^2/\bar{V}_1)(\phi_1 - \kappa_1)F(X) \quad (5)$$

Here, \bar{v} is the partial specific volume of the polymer, \bar{V}_1 the partial molar volume of the solvent, and $F(X)$ a factor standing for the molecular-weight dependence of A_2 . Substitution of the experimental values for A_2 , ϕ_1 , κ_1 , and so on at 25.5°C into eq. (5) leads to $F(X) = 1.04$. In the usual approximation that the ratio \bar{v}^2/\bar{V} is independent of temperature, A_2 may be expressed as follows:

$$A_2(T) = 6.76 \times 10^{-3} \{ \phi_{1,L}(1 - \Theta_L/T) \\ - (5.74\phi_{1,L} + 0.73) \{ \ln(\Theta_L/T) + (1 - \Theta_L/T) \} \} \quad (6)$$

This equation describes explicitly the temperature dependence of $A_2(T)$ by use of a parameter, $\phi_{1,L}$. The value of $\phi_{1,L}$ can be determined so that the above equation may allow to predict the observed dependence of A_2 on temperature satisfactorily. Such an optimization yields the value of -0.22 for $\phi_{1,L}$. The negative sign for $\phi_{1,L}$ is rational, since in an LCST region, polymer molecule having large M precipitates at lower temperature than does polymer molecule having small M . The fact that its absolute value is less than unity is also reasonable when compared with those in literature. With use of this value for $\phi_{1,L}$, the theoretical prediction of eq. (6) is illustrated by solid line in Fig. 2. In addition, the experimental data of A_2 are plotted therein. Naturally, the line fits the experimental data well, passing the point of $A_2 = 0$, in the elevated temperature region, at $t = 160^\circ\text{C}(\Theta_L)$. On

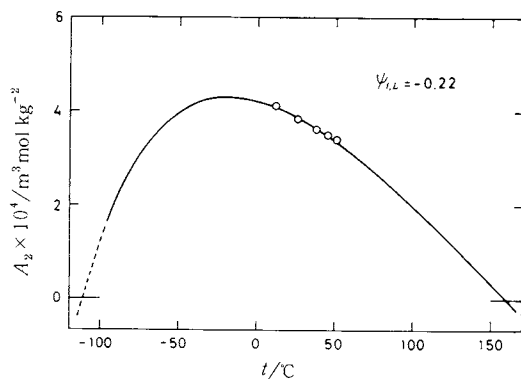


Fig. 2. An illustrative representation of eq. (6) for $A_2(T)$. Circles stand for the experimental data.¹⁰⁾

the contrary, one can see in the low temperature region that A_2 is predicted to vanish at -111°C . It should be noticed, however, that the freezing point of acetone is -95.4°C . Therefore, Fig. 2 shows that in practice, A_2 cannot vanish before the freezing point of the solvent is attained. Accordingly, an appearance of LCST proves to be impossible, which substantiates the observed stability of acetone solutions of cellulose diacetate at low temperatures.

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〈書評〉

S. Sunner and M. Månsson 編 : Experimental Chemical Thermodynamics, Volume 1, Combustion Calorimetry, Pergamon Press, Oxford and New York, 1979, XXV + 428 ページ。

本書は熱化学関係の IUPAC の単行本としては Experimental Thermochemistry, Volume 1 (F. D. Rossini 編, 1956) と Volume 2 (H. A. Skinner 編, 1962) に続くもので、これらが燃焼熱測定を中心にするながらも、反応熱測定一般をカバーしていたのに対して、本書は燃焼熱測定に的をしぼっている点に一つの特色がある。

本書は次の 18 章から成る。1. 単位と物理量 (F. D. Rossini), 2. 燃焼カロリメトリーの基本原理 (S. Sunner), 3. 燃焼カロリメーターの較正 (C. Mosselman and K. L. Churney), 4. 燃焼カロリメトリーのテスト物質と補助物質 (J. D. Cox), 5. 測定量からの標準状態エネルギーの算出 (M. Månsson and W. N. Hubbard), 6. 不確定度の配当 (G. Olofsson), 7. 一次文献に燃焼熱データを発表する方法 (E. F. Westrum, Jr.), 8. 酸素ボンベカロリメトリーによる液体、固体有機化合物燃焼熱

測定の一般的技術 (A. J. Head, W. D. Good and C. Mosselman), 9. 非金属ヘテロ原子をもつ液体、固体有機化合物の燃焼 (A. J. Head and W. D. Good), 10. 金属および簡単な金属化合物の燃焼カロリメトリー (C. E. Holley, Jr. and E. J. Huber, Jr.), 11. 有機金属化合物の燃焼カロリメトリー (H. A. Skinner), 12. フッ素と他のハロゲン中での燃焼 (W. N. Hubbard, G. K. Johnson and V. Ya. Leonidov), 13. 酸素による気体化合物のボンベ内燃焼 (V. P. Kolesov), 14. 酸素フレイムカロリメトリー (G. Pilcher), 15. フッ素フレイムカロリメトリー (G. T. Armstrong and R. C. King), 16. 燃焼カロリメトリーの工業的利用 (O. Riedel and H. Vogl), 17. 燃焼カロリメトリーの新傾向, 17.1 アネロイド燃焼ボンベカロリメトリー (A. S. Carson), 17.2 燃焼ボンベカロリメトリーにおける少量化 (M. Månsson), 17.3 Tian-Calvet ミクロカロリメーターの燃焼熱測定への応用 (M. Laffitte), 18. 燃焼カロリメトリーの歴史 (E. S. Domalski)。

2 章と 3 章は燃焼カロリメトリーのエネルギー測定の側面についての理論的取扱いで、本書の中ではやや難解 (80 頁につづく)