

Thermodynamic Study on Acetone Solutions of Cellulose Diacetate by Rayleigh Light Scattering

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Rayleigh light scattering measurements were carried out on acetone solutions of a cellulose diacetate fraction at five different temperatures ranging from 12.6₁ to 50.3₄°C. The second virial coefficient A_2 was found to decrease almost linearly with increasing in temperature. After determining the temperature derivative of A_2 , the enthalpy parameter κ_1 and the entropy parameter ϕ_1 were estimated: $\kappa_1 = -0.10_8$ and $\phi_1 = -0.05_1$. The results obtained indicate that (i) the present system is exothermic, (ii) in view of the negative sign both for κ_1 and ϕ_1 , some specific interaction between solute and solvent is present, and (iii) acetone is a "configurationally" poor solvent, but is nevertheless a "thermally" good solvent for cellulose diacetate. The exothermic nature of the present system was considered from the standpoint of solvation due to hydrogen bonding.

1. INTRODUCTION

Light scattering is well known to be the unique method by means of which the size and shape of large molecules in solution can be determined. In the preceding paper,¹⁾ we reported its application to a study on the conformation of cellulose diacetate molecules in acetone solutions. Since the scattering intensity is related, as is shown in eq. (1), to the chemical potential of the solvent, light scattering is also one of the important tools for determining thermodynamic properties of solutions. The present article communicates the results of such a thermodynamic study on the system cellulose diacetate-acetone.

In general, the solubility of cellulose derivatives is limited to certain solvents and depends upon various factors such as the degree of substitution, chemical structure of solvent, procedure of dissolution, and so on.²⁾ Because they are partially crystalline, less flexible, and polar polymer molecules. Several types of solvation specific to the chemical structures of substitute and solvent must effect complete dissolution of cellulose derivatives.

This is obvious from a finding that the molecular characteristics of cellulose derivatives are by no means intrinsic to their structure, but do vary with solvent. Those specific interactions are discussed through the phenomenological thermodynamic parameters in the present study.

Thermodynamic data of the present system are available in the literature only in higher polymer concentration range. Jeffries³⁾ obtained from measurements of both vapour pressure depression and osmotic pressure a result that the heat of dilution was, though positive, very close to zero up to the polymer weight fraction of about 0.70 and then became definitely negative in the fraction range of 0.80 to 0.95. Moore and Shuttleworth⁴⁾ succeeded to measure vapour pressure depression and stated in their paper that their signs of both the heat and entropy of dilution differed from those given by Jeffries. However, the disagreement is only apparent. In actual, their results are consistent with those of Jeffries qualitatively. Yet some quantitative problems remain unsettled. Moore and Shuttleworth observed that the lowest polymer weight fraction at which the heat of dilution became negative was as low as 0.2. In view of a fact that errors are likely to be great at lower concentrations in this type of measurement of the solvent activity, it seems appropriate

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to adopt Rayleigh light scattering which affords us thermodynamic information of dilute solutions with accuracy.

2. THEORETICAL

According to the fluctuation theory of light scattering, the reduced intensity of scattering, i.e., the Rayleigh ratio $R(0, c)$ and the difference of chemical potentials per mole between the solvent in solution and in pure phase $\Delta\mu_1$ are interrelated by the following equation:

$$\frac{Kc}{R(0, c)} = \frac{1}{RT\bar{V}_1} \left(-\frac{\partial \Delta\mu_1}{\partial c} \right)_{p, T} \quad (1)$$

Here, $R(0, c)$ denotes $\lim_{\theta \rightarrow 0} R(\theta, c)$, θ is the scattering angle, c the solute concentration (g/cm^3), K the familiar light scattering constant including the Cabannes factor of depolarization, \bar{V}_1 the partial molar volume of the solvent, p the pressure, R and T have the usual significance. Sometimes $\Delta\mu_1$ is called the partial molar Gibbs free energy of dilution. As the osmotic pressure Π has a relationship with $\Delta\mu_1$,

$$-\Delta\mu_1/\bar{V}_1 = \Pi = RTc(M^{-1} + A_2c + \dots) \quad (2)$$

equation (1) can be re-written as

$$Kc/R(0, c) = M^{-1} + 2A_2c + \dots \quad (3)$$

where M is the molecular weight of the solute molecules, and A_2 the second virial coefficient, whose dependence on temperature is characteristic of thermodynamic properties of the solution. Inasmuch as the terms higher than c^2 can be neglected for dilute solutions, one may express the second virial coefficient in the excess chemical potential of the solvent $\Delta\mu_1^E \equiv \Delta\mu_1 - RT \ln X_1$ (X_1 : the mole fraction of solvent):

$$A_2 = -\Delta\mu_1^E/RTc^2\bar{V}_1 \quad (4)$$

When the excess chemical potential of the solvent is splitted into an enthalpy term $\Delta\bar{H}_1$ (the heat of dilution, or relative partial molar Gibbs free energy) and an entropy term $\Delta\bar{S}_1^E$ (the excess relative partial molar entropy), the two corresponding terms for A_2 , $A_{2,H}$ and $A_{2,S}$, can be obtained in the forms of

$$A_2 = A_{2,H} + A_{2,S} \quad (5)$$

$$A_{2,H} = -\Delta\bar{H}_1/RTc^2\bar{V}_1 \quad (6)$$

$$A_{2,S} = \Delta\bar{S}_1^E/RTc^2\bar{V}_1 \quad (7)$$

These quantities can be evaluated by determining the temperature dependence of A_2 at constant pressure experimentally:⁵⁾

$$A_{2,H} = T\alpha A_2 - T(\partial A_2/\partial T)_p \quad (8)$$

$$A_{2,S} = A_2(1 - \alpha T) + T(\partial A_2/\partial T)_p \quad (9)$$

In the above equations, α stands for the coefficient of thermal expansion of the solvent. Once the values of $A_{2,H}$ and $A_{2,S}$ are determined, it becomes possible to estimate the enthalpy parameter κ_1 and the entropy parameter ϕ_1 in the Flory nomenclature⁶⁾ from the following relations:

$$\kappa_1 = -A_{2,H}\bar{V}_1/\bar{v}^2 \quad (10)$$

$$\phi_1 = A_{2,S}\bar{V}_1/\bar{v}^2 \quad (11)$$

Here, \bar{v} is the partial specific volume of the solute molecules. The above equations afford a practical way of the estimation of κ_1 and ϕ_1 in the range of very low concentrations.

3. EXPERIMENTAL

3.1 Polymer sample and solvent

A cellulose diacetate fraction coded as EF3-8 was employed in this study. The detailed description on the starting material, the procedures of acetylation reaction and successive solution fractionation have already given elsewhere.⁷⁾ The molecular characteristics of this fraction are as follows: the weight-average molecular weight M_w as determined by light scattering is 9.49×10^4 , the ratio of molecular weights M_w/M_n (M_n : the number-average molecular weight) as determined by gel permeation chromatography is 1.31, and the limiting viscosity number $[\eta]$ is $154 \text{ cm}^3/\text{g}$ in acetone at 25.0°C .

A guaranteed grade acetone (Nakarai Chemicals Co., Kyoto) was dried over molecular sieves 4A and then fractionally distilled through an efficient column.

3.2 Light-scattering photometry

Use was made of a Fica 50 light scattering

photometer (Sofica, Paris). The light scattered from the sample molecules in acetone was measured at five different temperatures ranging from $12.6_1 \pm 0.0_5$ to $50.3_4 \pm 0.1_5$ °C with blue (436 nm) light. Vertically polarized components of the light were used both for illumination and detection. The photometer was calibrated at 25°C against benzene (spectroscopy reagent) by using the literature values,⁸⁾ $46.4 \times 10^{-4} \text{ m}^{-1}$ for the Rayleigh ratio and 0.42 for the depolarization ratio ρ_u of the unpolarized light. The conversion of the Rayleigh ratio value from that for unpolarized light to that for polarized light was carried out by multiplying the former by the factor $(2 - \rho_u)/(1 + \rho_u)$.

The scattered-light intensity corrected for the scattering volume I was recorded at eleven scattering angles ranging from 30 to 150°. The ratio $I(\theta)/I(90^\circ)$ observed for pure benzene was found to be 1.000 ± 0.009 at each scattering angle, and no correction was necessary for the imperfectness of the optical system and the cylindrical glass cells used. Neither reflection correction was made, since the refractive index of vat liquid, xylene, was very close to that of the glass cells.

The sample solutions and the solvent were clarified by filtering them through a Sartorius Membranfilter SM 11607 of 0.2 μm pore diameter directly into cleaned glass cells, each of which is fitted with a ground-glass stopper. Light-scattering data obtained were analyzed by the usual double-extrapolation procedure of Zimm.⁹⁾ Five concentrations ranging from 0.077₈ to 0.388₈ $\times 10^{-2} \text{ g/cm}^3$ at 25.4₈ °C were employed in carrying out the analysis.

3.3 Specific refractive index increment

Refractive index increments of acetone solutions of the sample for blue light were measured on a Shimadzu DR-4 differential refractometer (Shimadzu, Kyoto). The apparatus was calibrated against aqueous potassium chloride. The specific refractive index increment dn/dc of the system was found to be fairly well represented by the relation

$$dn/dc = 0.112 + 3.3 \times 10^{-4} (t - 25^\circ)$$

where t is the temperature in Celsius.

4. RESULTS

Figure 1 illustrates the Zimm plots for the sample, cellulose diacetate fraction EF3-8 in acetone at 25.4₈ °C. Here, a negative value -250 for the plotting constant k is employed for a better spacing of points. Within the concentration range examined, points extrapolated with respect to the scattering angle are seen to fit closely to a straight line, allowing accurate determinations of an intercept of the ordinate and a slope. Since the sample is heterogeneous, the molecular weight as determined by eq. (3) becomes M_w . We got the value of $9.4_9 \times 10^4$ for M_w from this analysis.¹⁾ From the slope of the line, on the other hand, A_2 was estimated to be $3.8_5 \times 10^{-4} \text{ m}^3 \text{ mol/kg}^2$. Similar reticulate diagrams were obtained at the other four temperatures. It was found from the results of analysis that the values of M_w were coincident with each other within experimental error, showing that no association occurred in the solvent. Another point noticeable is that A_2 decreases with increasing in the temperature of measurements.

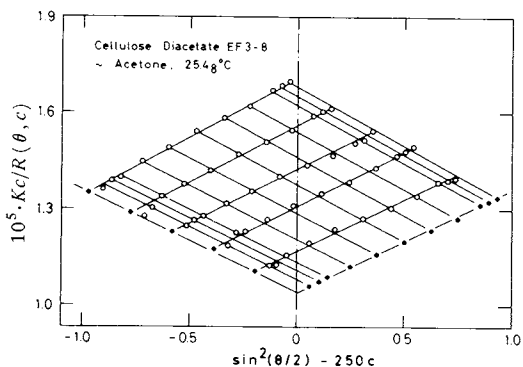


Fig. 1 The Zimm plots of light scattering data obtained with blue light for cellulose diacetate fraction EF3-8 in acetone at 25.4₈ °C.

Table I. Thermodynamic parameters of cellulose diacetate fraction EF3-8 in acetone

T °C	$A_2 \times 10^4$ $\text{m}^3 \text{ mol/kg}^2$	$A_{2,H} \times 10^4$ $\text{m}^3 \text{ mol/kg}^2$	$A_{2,S} \times 10^4$ $\text{m}^3 \text{ mol/kg}^2$
12.6 ₁	4.1 ₃	6.9 ₇	-2.8 ₄
25.4 ₈	3.8 ₅	7.1 ₆	-3.3 ₁
37.7 ₈	3.6 ₅	7.3 ₇	-3.7 ₂
45.0 ₀	3.5 ₀	7.4 ₇	-3.9 ₇
50.3 ₄	3.4 ₁	7.5 ₅	-4.1 ₄

All the experimental values of A_2 are listed in column two of Table I.

5. DISCUSSION

Figure 2 shows plots of A_2 against T . Within the limited range of temperature, A_2 may be approximately seen to decrease linearly, the temperature derivative $(\partial A_2/\partial T)_p$ at one atmosphere being evaluated to be -1.85×10^{-6} . This negative sign of $(\partial A_2/\partial T)_p$ suggests a possibility of appearance of lower critical solution temperature (LCST) and indicates that the solutions under study are exothermic. As stated in Introduction, the present system is known to be exothermic at high polymer concentrations. On that account it is interesting to see that at the extreme concentrations, very low or high, the heat of dilution is negative. The exothermic nature of the present system will be discussed later, and we first aim to determine the two thermodynamic parameters κ_1 and ϕ_1 .

Substituting the $(\partial A_2/\partial T)_p$ value determined above into eqs. (8) and (9), we calculated the enthalpy part and entropy part of A_2 . For the calculation, the literature value, $\alpha = 1.423 \times 10^{-3}$ was employed. The values thus estimated for $A_{2,H}$ and $A_{2,S}$ are listed in columns three and four of Table I. It is seen from those results that the values observed for A_2 may be ascribable predominantly to the enthalpy part of A_2 , while the contribution of its entropy part is negative, though small in absolute number. We next estimate the parameters κ_1 and ϕ_1 by using the values of $A_{2,H}$ and $A_{2,S}$ with eqs. (10) and (11). When the averaged literature value of v_2 ,⁹⁾ 0.692 for the present system is taken to convert c into the volume fraction X_2 ,

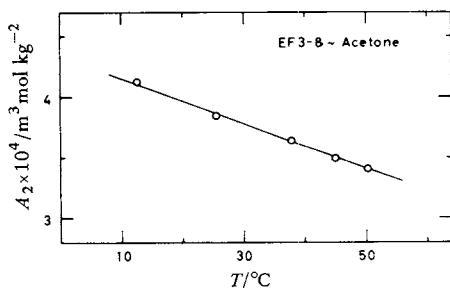


Fig. 2 Temperature dependence of A_2 for cellulose diacetate fraction EF3-8 in acetone.

the following results yield at 25.48°C :

$$\kappa_1 = -0.108 \text{ and } \phi_1 = -0.051.$$

Although theoretical considerations based on the lattice arrangement yield the approximate value of one-half for ϕ_1 ,^{11,12)} it has been well known that ϕ_1 's of real polymer solutions take values lower than the theoretical one and vary depending upon the chemical structure of the solvent used. For instance, the value as low as 0.006 was estimated for the system polystyrene-2-butanone.⁶⁾ However, the occurrence of negative value for ϕ_1 is unexpected. Because entropy should favour the mixing process in general. This finding elucidates, therefore, that dilution is accompanied with an ordering process which makes the excess entropy negative. Such a case is rather unusual, but has been reported on several polymer molecules such as poly(methacrylic acid),¹³⁾ polyacrylonitrile,¹⁴⁾ gelatin and collagen.¹⁵⁾ In those cases, strong interactions owing to the dipole moment and/or the hydrogen bonding play a significant role. It is known that negative sign both for κ_1 and ϕ_1 are the characteristics of exothermic solutions in which some specific interactions between the solvent and the solute molecules are present. From the two parameters determined, the thermodynamic quality of the solvent may be assessed: in view of a fact that ϕ_1 is negative, acetone is a "configurationally" poor solvent, but is nevertheless a "thermally" good solvent, for a negative value of κ_1 is found. In connection with the above assessment, it could be worthwhile to mention an interesting phenomenon that a mixture of cellulose triacetate with acetone can form a solution only when cooled to about -40°C or below and then warmed to ambient temperature with shaking.²⁾ Acetone must be much thermally better a solvent for cellulose triacetate than for cellulose diacetate.

The thermodynamic parameters are related to the Θ temperature as $\Theta = \kappa_1 T / \phi_1$. From this relation, the Θ temperature (in this case, LCST) may be calculated to be 358°C . This is only a rough estimate unverified experimentally. Here we would like to mention briefly the LCST phenomenon. At the time when LCST was first discovered for normal systems of hydrocarbon polymers-hydrocarbon solvents¹⁶⁾ and subsequent-

ly was recognized as a widespread phenomenon in polymer solutions, it had been considered for the time being that the (classical) Flory-Huggins theory of solution^{6,12)} had no ability of telling about this phenomenon as well as the volume change of mixing. However, it has been proved by Koningsveld¹⁷⁾ and Eichinger¹⁸⁾ that without ignoring the specific heat term, the Flory-Huggins theory does predict the LCST phenomenon. Since their studies have been referred to scarcely, a brief comment was given for appreciating the classical lattice theory of polymer solutions.

Now we consider the exothermic nature of the present system. Since the contacts between solute and solvent cause a heat change of solution, the heat of dilution, i.e., the partial molar heat of mixing should have the same sign as the heat of mixing of solvated polymer with solvent ΔH_m . In real solutions, various intermolecular forces may be supposed to work. They are due to dispersion, dipole orientation, dipole induction, hydrogen bond, and so on. When the interactions except the dispersion forces are absent, the heat of mixing is, as is well known, always positive or zero. Even if the interaction due to dipoles are included as an additional effect, no possibility can be found to predict evolution of heat.¹⁹⁾ A possible cause might be ascribed to hydrogen bonding. The trend of hydrogen bonding can be deduced by the electronic character of the substances in question. In other words, it may be appropriate to characterize the substances from the standpoint of the proton-donating and proton-attracting capacities.^{20,21)} When the proton-donating and proton-attracting powers of a liquid are expressed by two parameters σ and τ respectively, the cohesive energy due to hydrogen-bond formation is considered to be some function of σ and τ . Since the function is obviously zero when either σ or τ is zero, the product $\sigma\tau$ is the simplest such function. If in a liquid mixture, σ and τ should be added on a mole fraction basis, the contribution to the heat of mixing due to hydrogen-bonding effects is written as¹⁹⁻²²⁾

$$\Delta H_m = X_1 X_2 (\sigma_1 - \sigma_2) (\tau_1 - \tau_2) \quad (12)$$

Since acetone is a strong proton-attractor, it follows $\sigma_1 = 0$ and $\tau_1 > 0$. On the other hand, cellulose diacetate has a complex character: both

σ_2 and τ_2 are not zero due to the hydroxyl and acetyl groups respectively. It is obvious, however, that acetone is stronger a proton-attractor than the acetyl group in cellulose diacetate, i.e., $\tau_1 > \tau_2$. Substituting these relations into eq. (12), we find ΔH_m negative. This is only a qualitative explanation. However, it is plausible, for evidences of the solvation due to hydrogen bonding have been shown for cellulose diacetate in a number of solvents.²³⁻²⁶⁾ Proton-donors such as acetic acid, nitromethane, and *p*-cresol are bound by hydrogen bonds to acetyl groups, while proton-attractors such as aniline, pyridine, and α -picoline solvate hydroxyl groups, giving rise to breaking intramolecular hydrogen bonds between primary hydroxyl and acetyl groups on neighboring rings. These differences in the type of solvation may be understood to reflect the observed solvent dependence of the flexibility of cellulosic chain.^{2,7)} Hitherto we considered the solvation problem by use of only phenomenological results. Much more direct information will be obtained from suitable spectroscopic investigations. A study by nuclear magnetic resonance has been carried out and will be published elsewhere shortly.²⁷⁾

REFERENCES

- 1) H. Suzuki, Y. Miyazaki, and K. Kamide, *Europ. Polym. J.* in press.
- 2) See, for example, K. Kamide, Y. Miyazaki, and T. Abe, *Polym. J.* **11**, 523 (1979).
- 3) R. Jeffries, *Trans. Faraday Soc.* **53**, 1592 (1957).
- 4) W. R. Moore and R. Shuttleworth, *J. Polym. Sci. A-1*, 733 (1963).
- 5) G. V. Schulz, H. Inagaki, and R. Kirste, *Z. physik. Chem. (Frankfurt am Main)* **24**, 390 (1960).
- 6) P. J. Flory, "Principles of Polymer Chemistry", Cornell Univ. Press, Ithaca, New York (1953).
- 7) K. Kamide, T. Terakawa, and Y. Miyazaki, *Polym. J.* **11**, 285 (1979).
- 8) S. Claesson and J. Öhman, *Arkiv Kemi* **23**, 69 (1964).
- 9) B. H. Zimm, *J. Chem. Phys.* **16**, 1093 (1948).
- 10) V. M. Golubev and S. Ya. Frenkel, *Vysokomolekul. Soedin. A9*, 1847 (1967).
- 11) P. J. Flory, *J. Chem. Phys.* **10**, 51 (1942).
- 12) M. L. Huggins, *J. Phys. Chem.* **46**, 151 (1942); *Ann. N.Y. Acad. Sci.* **43**, 1 (1942).

- 13) A. Silberberg, J. Eliassaf, and A. Katchalsky, *J. Polym. Sci.* **23**, 259 (1957).
- 14) W. R. Krigbaum and N. Tokita, *ibid.* **43**, 467 (1960).
- 15) L. V. Rajagh, D. Puett, and A. Ciferri, *Biopolymers* **3**, 421 (1965).
- 16) P. I. Freeman and J. S. Rowlinson, *Polymer* **1**, 20 (1960).
- 17) R. Koningsveld, Thesis, University of Leiden (1967).
- 18) B. E. Eichinger, *J. Chem. Phys.* **53**, 561 (1967).
- 19) P. A. Small, *J. Appl. Chem.* **3**, 71 (1953).
- 20) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond", W. H. Freeman, San Francisco, Calif. (1960).
- 21) H. Renon, C. A. Eckert, and J. M. Prausnitz, *Ind. Eng. Chem. Fund.* **6**, 52 (1967).
- 22) H. Burrell, *Adv. Chem. Ser. No. 124*, 1 (1973).
- 23) F. Howlett and A. R. Urquhart, *Chem. & Ind.* **82** (1951).
- 24) W. R. Moore and J. Russell, *J. Colloid Sci.* **8**, 243 (1953).
- 25) W. R. Moore and J. Russell, *J. Appl. Chem.* **4**, 369 (1954).
- 26) W. R. Moore, J. A. Epstein, A. M. Brown, and B. M. Tidswell, *J. Polym. Sci.* **23**, 23 (1957).
- 27) K. Kamide and K. Okajima, unpublished results and will be submitted to *Polym. J.*

アメリカ金属学会のシンポジウム 「合金相の相図計算と熱化学」に招かれて

(東大工学部) 高橋 洋一

金属物理化学の分野で、合金相に関する最近の理論・実験の両面での進展は著しい。昨秋、米国金属学協会の秋季大会の期間中に、AIMEの冶金部会と、TMS(米国金属学会)の熱力学委員会の共催で、合金相の相図計算・熱化学に関するシンポジウムが開催されたのも、その一つの反映であろう。私も、旧知のAmes研究所・J. F. Smith博士がこの計画の責任者であったことから、理論・実験にわたる4つのセッションのうちの「実験技術」での講演を依頼され、9月17-19日のミルウォーキでのシンポジウムに参加することになった。

このシンポジウムはすべて招待講演(16件)のみで構成され、一般研究発表は含まれていない。これは、表記のテーマについて特に物理・化学の両側面から平常はあまり顔を合わすことのない専門家の間で十分議論して、相互理解を深めよう、という世話人の意向によるもので、出席したのは米国を中心に、カナダ・西ドイツ・スウェーデンなど、国際的ながら40人ほどの小じんまりした会合であった。日本からは、私のほかは、現在シカゴ大に留学中の横川晴美博士(化技研)のみであった。

内容については、私の専門外の面が多く、具体的には早速に刊行された予稿集(Calculation of Phase Diagrams and Thermochemistry of Alloy Phases ed. J. F. Smith, Y. A. Chang, The Metallurgical Society of AIME)があるので、必要ならば御照会いただければよいが、私にも面識のあるLeo Brewer, J. F. Elliott, O. J. Kleppa各博士などの講演は大変興味深く、啓発されるところがあった。私に課せられたのは、例のレーザーフラッシュカロリメトリーと、金属の熱容量データの再評価についての報告で、Pt, Au, Thなど、比較的身近な金属の熱容量のデータが、特に室温付近で問題があり確立されていないこと、レーザー法のデータで再検討した結果修正すべきもののあることを述べた。

この会合に出席することができたのは、吉田科学技術財団の旅費の御援助を得ることができたからである。何かとお世話になった松本直史氏および財団に深謝する次第である。