Cloud-Point Curves of Ternary System Nitroethane + Cyclohexane + Polystyrene Determined by a Novel Method

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ABSTRACT: A λ -shaped cell made with main and side tubes had been used to determine cloud-point curves (CPCs) of the ternary system nitroethane (NE) + cyclohexane (CH) + polystyrene (PS) by visual observation. Without being exposed to air, PS ($M_w = 4.8 \times 10^4$) in the main tube was diluted by the mixed solvent in the side tube step by step by inclining the cell. This novel device eliminated scattering of cloud-point data due to impurities. The observed CPCs at constant composition of the mixed solvent have been converted into CPCs at constant compositions of PS and binodals on a composition triangle. The cloud-point temperatures of the binary system NE + PS decreased rapidly by the presence of small amounts of CH, indicating cosolvency. The cloud point temperatures of CH + PS increased by the presence of NE. The latter behavior could vary depending on the molecular weight of PS. The cloud-point temperatures near the critical composition of NE + CH decreased by the addition of PS.

KEY WORDS Polystyrene / Mixed Solvent / Cloud Points / Binodals /

To determine the cloud-point curve (CPC) of a binary liquid mixture by a visual method, a number of solutions of different compositions must be prepared and sealed in clean glass tubes with extreme care to avoid contamination with impurities, because even very slight amounts of impurities cause scattering of data points. To avoid moisture in the air, solution preparation and transfer of solutions into tubes must be carried out in a glove box under a dry nitrogen atmosphere.^{1,2} For a ternary mixture many CPCs must be measured with the same care as in the case of binary mixtures to determine the binodal surface.

In a previous study,³ we have devised a cell to determine cloud points for the binary system nitroethane + cyclohexane. The cell was made of a main tube with a side tube (see Figure 1) and named "lambda" cell after its form. The experimental procedure was as follows. A small amount of weighed nitroethane was introduced into the main tube, and cyclohexane was put into the side one. By inclining the cell,

cyclohexane in the side tube was transferred step by step into the main tube to prepare solutions. At each step, a cloud-point determination was carried out by visual observation.

With the lambda cell method, solutions for CPC can be prepared in a closed cell without being exposed to the air and, therefore, scattering of the data points due to impurities can be eliminated. Moreover, CPC can be determined by using a single cell, in contrast to conventional cloud-point experiments, in which the preparation of many sample tubes is laborious and time-consuming. It should be noted that the amount of sample used for determining a CPC is much smaller in the lambda cell method than in the conventional one. These features of the lambda cell method are very favorable to the study of binodals of ternary liquid mixtures. It should be also mentioned that the lambda cell method could be applicable to experiments of other transition phenomena such as a sol-gel transition.

In this study we have carried out cloud-point

EXPERIMENTAL

Materials

Reagent grade cyclohexane, after being passed through silica gel, was fractionally distilled in a 1.8×100 cm column packed with Raschig rings and covered with an evacuated jacket. A fraction boiling at constant temperature was stored in a flask sealed with a teflon cap. Nitroethane was dried over calcium chloride and fractionally distilled at reduced pressure under nitrogen gas. A middle fraction at constant boiling temperature was sealed in a flask and stored in a desiccator in the dark. No impurity was detected for the liquid samples by gas chromatography. Polystyrene of $M_w = 50000$ and $M_w/M_n < 1.06$ was obtained from the Pressure Chemical Company, Pittsburgh and purified by solution fractionation, where M_w and M_n are the weight and number-average molecular weight, respectively. The molecular weight M_w of the sample used was found to be 4.8×10^4 by a light scattering measurement.

Figure 1. Lambda cell for measurements of cloud points. The polystyrene solution in the main tube of 0.8 cm i.d. can be diluted step by step with the mixed solvent in the side tube of the same size by inclining the cell.

experiments on the ternary system nitroethane (NE) + cyclohexane (CH) + polystyrene (PS) to establish the lambda cell method and to present a new type of binodal behavior. The binary system NE + CH has been found to have a critical point at 22.9°C and at 0.65 in volume fraction of CH.³ PS is partially soluble in NE and in CH. CPCs for the present ternary system were determined by using the lambda cell in which PS in the main tube was diluted with mixed solvent in the side one. The obtained CPCs were converted into CPCs at constant PS composition and then to binodals on a composition triangle. Near the critical composition of the mixed solvent, the cloud-point temperature decreased with increasing PS composition, contrary to the behavior of other ternary systems of polymer in mixed solvent.⁴⁻⁹

CPC Measurements

The lambda cell as shown in Figure 1 was used for cloud-point measurements. The cell consists of a main tube of 0.8 cm inside diameter and 20 cm length and a side one of the same size. A teflon-coated stirrer is set in each of the tubes. We calibrated the meniscus height of liquid in the main tube against the volume of the liquid. For this purpose, cyclohexane of various amounts was put into the main tube by an injector. The meniscus height from the bottom of the main tube was measured by a cathetometer and the volume was determined by weighing. This calibration was used to determine the composition of solutions in the main tube. In the previous study on the system NE + CH,³ we used a lambda cell with a main tube of 0.5 cm inside diameter. Since the refractive index difference between NE and CH is as small as 0.033, cloud points were not easy to determine by eye in that cell. The main tube of the larger inside

diameter used in this study made possible a better determination of cloud points.

To determine CPC at a constant composition of the mixed solvent NE + CH, a PS sample of about 0.03 g was put into the main tube, dried in vacuum and weighed. Then the mixed solvent of known composition was introduced into the side tube and the cell was sealed by a teflon tube and a glass cap after being filled with dry nitrogen gas. The PS sample in the main tube was diluted step by step with the mixed solvent from the side one. At each step, the cell was immersed in a water bath, the temperature of which was controlled to 0.01 K. The bath temperature was monitored by a quartz thermometer with a precision of ± 1 mK and the cloud-point temperature was determined based on a mercury-in-glass thermometer calibrated to 0.01 K. The solution in the main tube was completely homogenized above the phase separation temperature by a stirrer. To observe abrupt change of turbidity or optical homogeneity in the solution, the temperature of the water bath was lowered or raised at a rate of about 0.01 K min^{-1} . When change was not clearly visible, the solution was kept at a constant temperature to observe an occurrence of phase separation. In this way, the cloud-point temperature, at which a sudden change occurred in optical homogeneity of the solution, was reproduced within $\pm 0.02 \text{ K}$. The volume fraction of PS of the solution in the main tube could be estimated from the weight of PS and the meniscus height of the solution.

By regulating the volume of the mixed solvent transferred from the side tube at each step, cloud-point temperatures could be determined at suitable intervals of the PS volume fraction ϕ_3 . A single run, which was carried out in a day, gave CPC in the range of ϕ_3 from 0 to 0.1. The cloud-point temperature of the mixed solvent in the side tube was measured at the beginning and at the end of each run to test for any composition change of the mixed solvent caused by preferential migration of the solvent vapor between the two

tubes. The difference of these two cloud-point temperatures was less than 0.05 K, which was negligibly small compared with the large variation of the cloud-point temperature with the PS volume fraction.

RESULTS

In the present cloud-point measurements, primary compositions are the volume fraction u_2 of CH in the mixed solvent based on pure state and the mass concentration c_3 of PS, from which the volume fractions of CH and PS are calculated, respectively, by the equations

$$\phi_2 = (1 - \phi_3)u_2 \quad (1)$$

$$\phi_3 = v_3 c_3 \quad (2)$$

where v_3 is the specific volume of PS and the value $v_3 = 1.0742 \text{ g ml}^{-1}$ at 20°C was used.¹⁰ Excess volume on mixing of PS with the mixed solvent causes little uncertainty in the estimation of volume fractions and does not affect the behavior of CPCs, because the partial specific volume of PS is usually very close to its specific volume.¹¹

We have determined 18 CPCs for different values of u_2 and CPC for the binary system NE + CH. Figure 2 shows the cloud-point data for NE + CH obtained with NE in the main tube and CH in the side one.³ The open circles, which were determined with four experimental runs, yield a well-defined CPC. From the intersection of the CPC and the diameter given by the broken line the critical point was determined as $u_2 = 0.655$ and $t = 22.9^\circ\text{C}$, which agreed with the previous ones.³ The binary system CH + PS was found to have a critical point at $\phi_3 = 0.107$ and $t = 14.8^\circ\text{C}$ from the top of the CPC. The critical point for the binary system NE + PS was located near $\phi_3 = 0.125$ and $t = 29.9^\circ\text{C}$.

In Figures 3 and 4 some of the observed CPCs are represented by the plot of temperature versus ϕ_3 . The cloud-point temperatures listed in Table I were read from the observed

Figure 2. Cloud-point curve for the binary system nitroethane+cyclohexane in a temperature-volume fraction u_2 diagram. The open circles were obtained by four experimental runs with the lambda cell. The filled circles indicate cloud-point temperatures at $\phi_3=0$ in Table I. The broken line indicates diameter.

Figure 3. Cloud-point curves for the ternary system nitroethane+cyclohexane+polystyrene at constant volume fractions u_2 of cyclohexane in the mixed solvent in a temperature-volume fraction ϕ_3 diagram, with ϕ_3 being the volume fraction of polystyrene. The curves a, b, c, and d were determined at $u_2=0.038, 0.109, 0.298$, and 0.509 , respectively.

Figure 4. Cloud-point curves for the ternary system nitroethane+cyclohexane+polystyrene as in Figure 3. The curves a, b, c, d, and e were determined at $u_2=0.662, 0.797, 0.848, 0.894$, and 0.937 , respectively.

CPCs. In Figure 3 the cloud-point temperature at $u_2=0.038$ and 0.109 increases with increasing volume fraction ϕ_3 as in the case of a polymer in a single solvent, while at $u_2=0.298$ and 0.509 the CPCs change in the opposite

Table I. Cloud-point temperature in °C read from measured cloud-point curves

u_2	ϕ_3								
	0	0.01	0.02	0.03	0.04	0.05	0.06	0.08	0.10
0				25.98	27.43	28.40	29.04	29.66	29.91
0.038				18.08	19.52	20.51	21.12		
0.109				6.11	7.56	8.46	9.06		
0.298		8.56	7.85	7.12	6.36	5.58	4.66		
0.396	17.80	17.25	16.68	16.11	15.54	14.96	14.38	13.05	
0.493	21.49	21.32	21.04	20.69	20.28	19.78	19.22	18.05	16.90
0.509	21.80	21.55	21.27	20.97	20.63	20.24	19.81	18.80	17.52
0.546	22.44	22.20	21.91	21.59	21.24	20.87	20.50	19.69	18.63
0.591	22.77	22.60	22.40	22.17	21.93	21.65	21.35	20.64	19.84
0.662	22.83	22.62	22.44	22.28	22.13	21.97	21.80	21.35	20.81
0.707	22.82	22.55	22.33	22.18	22.09	22.00	21.89	21.56	21.15
0.749	22.57	22.43	22.29	22.18	22.08	21.99	21.90	21.67	21.37
0.797	21.75	21.97	22.01	21.98	21.94	21.88	21.82	21.67	21.49
0.848	18.94		21.46	21.60	21.62	21.62	21.59	21.51	21.39
0.894	13.96		20.80	21.09	21.21	21.25	21.24	21.13	20.92
0.937			19.44	19.87	20.09	20.16	20.15	20.00	19.77
0.978			15.86	16.55	16.96	17.15	17.21	17.17	17.03
1			12.46	13.48	14.02	14.37	14.59	14.79	14.81

direction. An inversion is expected to occur between $u_2=0.109$ and 0.298 , where the cloud-point temperature was too low to observe. The CPCs in Figure 4 were obtained for the volume fraction u_2 larger than the critical one for NE+CH. The curve at $u_2=0.662$ near the critical one decreases monotonically with increasing volume fraction ϕ_3 . The curves at $u_2=0.894$ and 0.937 behave similarly to that of a polymer in a single solvent. The cloud-point temperatures at $\phi_3=0$ for the curves at $u_2=0.509$, 0.662 , 0.797 , and 0.848 in Figures 3 and 4 were determined for mixed solvents in the side tube. In Figure 2 these cloud points are given by the filled circles, which agree with the CPC described by a solid line. This means that binodals can be directly constructed from the observed CPCs without any temperature adjustment.

Cloud-point temperatures at constant ϕ_3 given in Table I are plotted against u_2 in Figure 5. The solid curve and dot-dash curve are obtained at $\phi_3=0.03$ and 0.06 , respectively. The open circles for the solid curve represent the values read from the measured CPCs. The

Figure 5. Cloud-point curves for the ternary system nitroethane+cyclohexane+polystyrene in a temperature-volume fraction u_2 diagram at constant volume fractions ϕ_3 of polystyrene with u_2 being the volume fraction of cyclohexane in the mixed solvent. The broken, solid, and dot-dash curves were obtained at $\phi_3=0$, 0.03 , and 0.06 , respectively. The circles represent data at $\phi_3=0.03$ read from graphs in Figures 3 and 4.

Figure 6. Cloud-point curves for the ternary system nitroethane + cyclohexane + polystyrene as in Figure 5. The curves a, b, c, d, e, and f were obtained at $\phi_3 = 0, 0.02, 0.04, 0.06, 0.08$, and 0.10 , respectively.

broken curve is the CPC for the mixed solvent NE + CH. The part of $u_2 > 0.4$ in Figure 5 is depicted in enlarged scale in Figure 6. The curves a, b, c, d, e, and f are reproduced from Table I for $\phi_2 = 0, 0.02, 0.04, 0.06, 0.08$, and 0.10 , respectively. The crowded curves at the side of $u_2 = 1$ correspond to the small dependence of the CPC's on u_2 as shown in Figure 4. To construct binodals on a composition triangle, values of u_2 at constant temperatures were read from each curve in Figure 6. The volume fraction ϕ_2 was estimated from the values of u_2 and ϕ_3 by using eq 1. Thus, the binodals were obtained as in Figure 7, where the curves a, b, c, and d are at $22.0, 21.5, 20.0$, and 16.0°C , respectively. The two filled circles P_1 and P_2 on the edges represent the critical point for the binary systems.

DISCUSSION

It has been suggested that mixed solvents acquire enhanced solvent power for polymers, when the mixtures have a large excess free energy of mixing.¹²⁻¹⁵ Since the excess free energy of the mixture NE + CH is large, as

Figure 7. Binodals for the ternary system nitroethane (NE) + cyclohexane (CH) + polystyrene (PS) in a composition triangle with ϕ_2 and ϕ_3 being the volume fractions of CH and PS, respectively. The curves a, b, c, and d were obtained at $22.0, 21.5, 20.0$, and 16.0°C , respectively. The filled circles P_1 and P_2 represent the critical points for the binary systems NE + CH and CH + PS, respectively.

demonstrated by the miscibility gap, the mixture is expected to have high solubility with PS. From the behavior of the CPCs in Figure 5, NE is found to gain an enhanced solvent power by the addition of a small amount of CH. On the other hand, the cloud points near $u_2 = 1$ increase by the addition of NE. The rapid depression of the CPCs near $u_2 = 0$ could be understood as cosolvency^{16,17} and the behavior of the CPCs near $u_2 = 1$ gives the appearance of co-nonsolvency.⁹ However, the behavior of the CPCs near $u_2 = 1$ may depend

strongly on the molecular weight of PS, because the system CH + PS for $M_w > 2 \times 10^5$ has a critical temperature higher than that for NE + CH. Therefore, CPCs for large molecular weight are expected to show different behavior near $u_2 = 1$ from that of the CPCs in Figure 5. To elucidate the co-nonsolvency, it is necessary to investigate the second virial coefficient near $u_2 = 1$ as a function of molecular weight.

The phase-separation behavior of the present system can be well understood by binodals on the composition triangle given in Figure 7. The binodals spread out from the critical point P_1 on the NE-CH edge with decreasing temperature and touch the CH-PS edge at the critical point P_2 . This could mean that a critical line monotonically runs down from P_1 to P_2 , when the temperature axis is taken vertically to the composition triangle.

It is relevant to compare the present study with that for the ternary system *N,N*-dimethylformamide (DMF) + CH + PS ($M_w = 110000$) made by Wolf and Willms.⁹ Their system is different from ours only in one component. DMF is a good solvent for PS and its mixture with CH has a critical point at 48.6°C. They showed that the critical line from the DMF-CH edge to the CH-PS edge in the composition triangle has a maximum point of 51.3°C. This implies that binodals form a closed loop between 48.6 and 51.3°C. Binodals near the CH-PS edge ran parallel with the edge as in the case of Figure 7. The behavior of the binodals of the present system is rather simple compared with that of the system DMF + CH + PS. However, it should be remembered that the critical temperature of the system CH + PS can become higher than that of the system NE + CH, depending on the molecular weight. Thus, the critical line for the present system NE + CH + PS could behave in a different way for a different molecular weight PS.

In studies of the ternary system polymer + mixed solvent, much interest has been taken in CPC at the critical composition of the

mixed solvent. Dondos *et al.* have investigated several ternary systems and shown that the presence of polymer as a third component always raised the cloud-point temperature near the critical composition of the mixed solvent.⁴⁻⁹ The closed-loop binodals for DMF + CH + PS also indicate increase of the cloud point of the system DMF + CH by the presence of PS. In the present ternary system the cloud point near the critical point of the system NE + CH decreased with the addition of PS. In the ternary systems employed by Dondos *et al.*, the polymers have different solubilities in the component solvents, *i.e.*, one solvent is a good solvent and the other is a theta or nonsolvent, while the solubilities of PS in NE and CH are comparable, as indicated by the critical temperatures. Therefore, the behavior of the CPCs near the critical point of the mixed solvents observed by Dondos *et al.* and those observed by us are in accord with an old rule found by Timmermans,¹⁸ which is summarized as follows: the critical point of a binary system is mostly raised by the addition of a third component when it has very different miscibility with the components of the binary system, and is lowered when it is equally miscible with both the components. The rule of Timmermans has been justified by theories based on regular solutions.¹⁹⁻²¹ For ternary systems of polymer + mixed solvent it has been recognized that the ternary function makes a large contribution to the free energy of mixing.^{11,13} Accordingly, a theoretical prediction of CPCs can not be made reasonably, unless the ternary function as well as binary interaction functions are known as a function of temperature and compositions from experiments.

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