Bull. Chem. Soc. Jpn., ***68***, *2021—2023(1995)*

Effect of a Liquid–Liquid Phase Separation on the Slopes of Density vs. Concentration Plots

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(Received January 26, 1995)

The densities were measured for dextran (Dex)–polyethylene glycol (PEG)–water, poly(1-vinyl-2-pyrrolidone (PVP)–PEG–water, and poly(vinyl alcohol) (PVA)–PEG–water systems. In all cases, the linear relationship of the density vs. concentration plots was not affected by the occurrence of liquid–liquid phase separation. The partial specific volumes were calculated from the slopes of the straight lines of the density.

Liquid–liquid phase separations have been widely investigated by many investigators.[1] However, there has been no report concerning density measurements of solutions in which a phase separation occurred. We are interested in the effect of the phase separation on the slope of the density (ρ) vs. concentration (C) plots.[2,3]

The densities of polymer–polymer–water systems were measured over a wide range of concentrations up to high concentrations, where a liquid–liquid phase separation occurred. We could clarify the effect of the occurrence of phase separation on the slopes of ρ vs. C plots. The densities of PEG, Dex, and ethylene glycol were measured by other authors.[5,6]

Experimental

Materials. PVA (PVA-105: degree of saponification, 98.5 mol%), PVP and PEG were purified by reprecipitation in water–acetone, water–acetone and benzene–acetone, respectively. Dextran (Dex) was used without purification. The characteristics of the polymer samples are given in Table 1.

Measurements of Density. A Lipkin–Davison pycnometer was used to obtain the density. Measurements of the density were performed at 30 °C±0.01 °C over a wide range of concentrations up to high concentrations, where a liquid–liquid phase separation occurred. A solution in which a liquid–liquid phase separation had occurred was injected into the pycnometer with careful stirring. The marks (●, ■, and ▲) in the figures represent the phase separation. Before density measurements, the aqueous solutions of polymers were filtered through a membrane filter (pore size of 0.45 μm) in order to separate dust and undissolved gels. The concentrations (g cm^{-3}) of polymer mixtures in aqueous solutions were calculated from the weight fractions (g g^{-1}) which had been measured. The weight ratios of PVA/PEG,

Table 1. Characteristics of the Polymer Samples

Polymer	M_w	Supplier
PVA	24000	Kuraray Co., Ltd.
PVP	360000	Kishida Chemical Co., Ltd.
Dex	75000	Wako Pure Chemical Industries, Ltd.
PEG	20000	Kishida Chemical Co., Ltd.

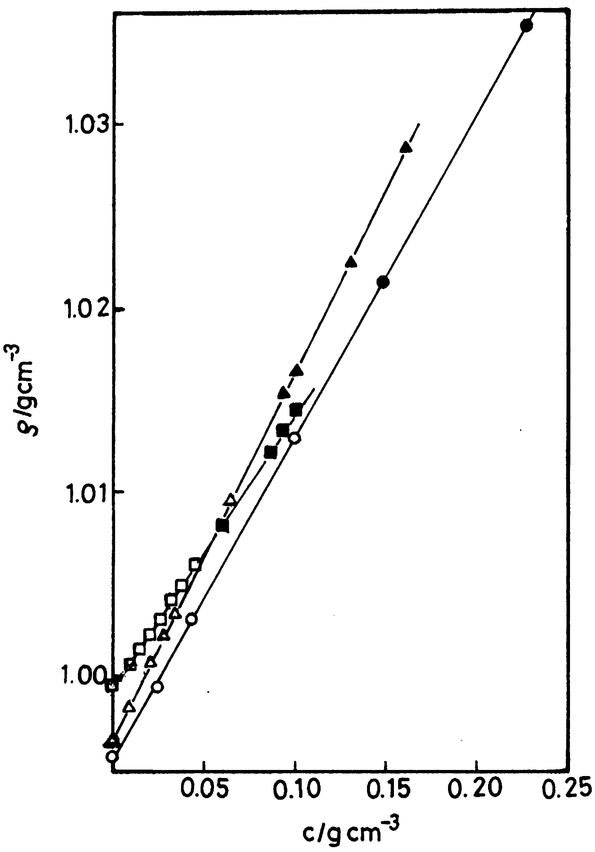

Fig. 1. Density vs. polymer concentration plots for PVP–PEG–water (○), PVA–PEG–water (□), and Dex–PEG–water (△) systems at 30 °C. weight ratio PVP/PEG=PVA/PEG=Dex/PEG=1/3 The marks ●, ■, and ▲ represent a liquid–liquid phase separation.

PVP/PEG, and Dex/PEG in the solutions were 1/3, 1, and 3 in each of the polymer mixtures. Also, for polymer–water systems, the densities were measured. The thus-obtained density in this experiment was estimated to be precisely within ±0.00005 g cm^{-3}. The partial specific volumes ($\overline{v}$) were calculated from the slopes of the straight lines of the density given in Fig. 1. Also, the densities of the upper and lower phases in some systems were measured. The results are given in Table 2.

Results and Discussion

Figure 1 shows ρ vs. C plots for the PVA–PEG–water, PVP–PEG–water, and Dex–PEG–water systems, which have a polymer ratio of 1/3. The results for polymer ratio of 1 and 3 are similar to that shown in Fig. 1, but are not shown. The density increased linearly with increasing polymer concentration in all cases. It is interesting that the linear relationship was retained even at high concentration, where a liquid–liquid phase separation occurred in all cases. These results mean that the overall density of a polymer mixture solution is not affected by the separation of the solution into two phases having different densities, namely the upper and lower phases.

It is generally considered that the density of a polymer solution increases along with increasing the amount of hydrated water, since the density of hydrated water is greater than that of ordinary water.[4] It can therefore be inferred in the present work that the phase separation does not affect the amount of hydrated water in solutions with different polymer ratios. When a liquid–liquid phase separation occurs, a change in the conformation of polymer chains is considered to occur. Therefore, it probably does not affect the amount of hydrated water in a random coil of the polymer chains. This is the reason why the linear relationship of ρ vs. C plots is retained after phase separation occurs.

Table 2 shows the densities of the upper and lower phases of polymer solutions, where a liquid–liquid phase separation occurs. It can be seen in Table 2 that the density of the lower phase is greater than that of the upper phase.

Figures 2, 3, and 4 show the polymer composition dependencies of the partial specific volume ($\overline{v}$) for

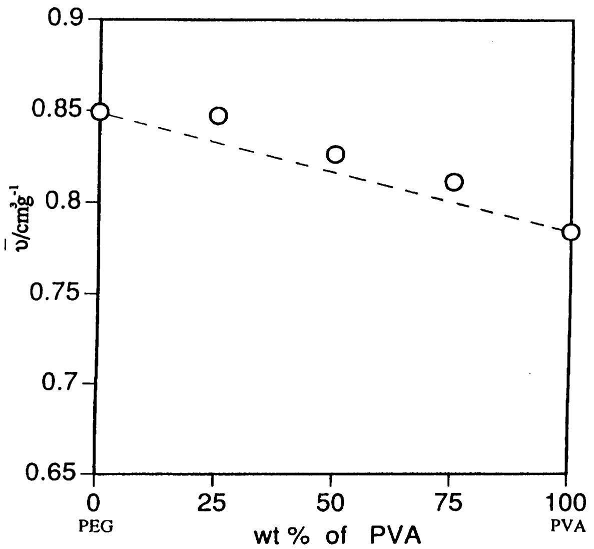

Fig. 2. Polymer composition dependence of partial specific volume for PVA–PEG–water system at 30 °C.

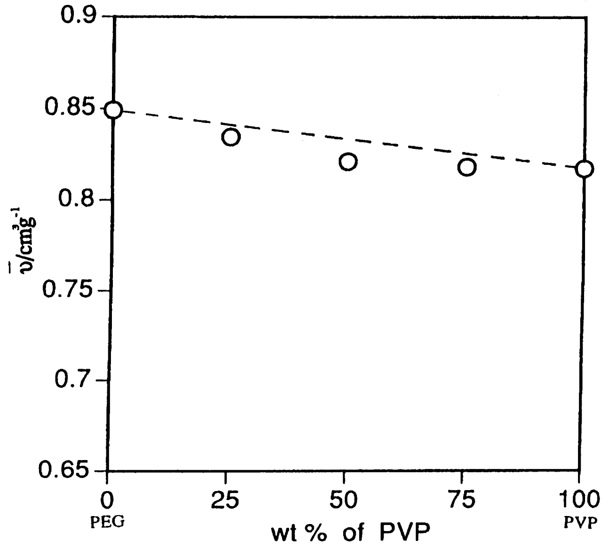

Fig. 3. Polymer composition dependence of partial specific volume for PVP–PEG–water system at 30 °C.

Table 2. Densities of Upper Phase and Lower Phase

Polymer	Weight fraction	Density at mixing	Density of upper phase	Density of lower phase
PVA/PEG =1/3	0.1049	1.0141	1.0117	1.0386
PVA/PEG =1	0.0898	1.0131	1.0091	1.0258
PVA/PEG =3	0.0860	1.0130	1.0087	1.0165
PVP/PEG =1/3	0.1917		1.0255	1.0525
PVP/PEG =1	0.1901	1.0306	1.0226	1.0430
PVP/PEG =3	0.2555		1.0286	1.0561
Dex/PEG =1/3	0.1279		1.0168	1.0821
Dex/PEG =1	0.1471	1.0362	1.0186	1.0796
Dex/PEG =3	0.1500	1.0442	1.0185	1.0635

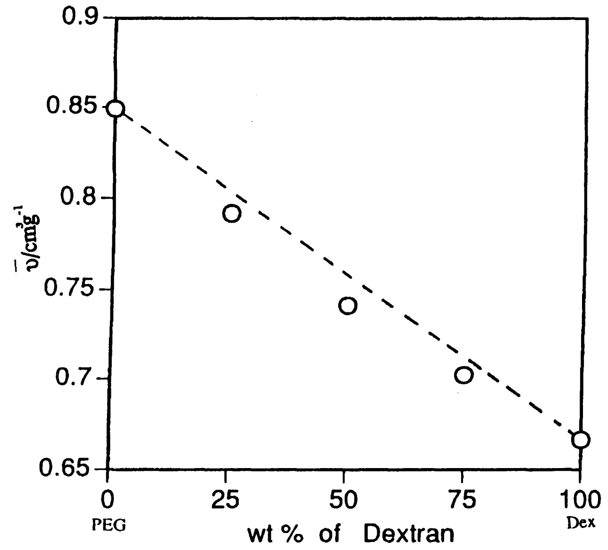

Fig. 4. Polymer composition dependence of partial specific volume for Dex–PEG–water system at 30 °C.

PVA–PEG–water, PVP–PEG–water, Dex–PEG–water systems, respectively. The partial specific volumes of the PVA–PEG–water system are larger than the line of additivity of the partial specific volume. Those of the PVP–PEG–water and Dex–PEG–water systems are smaller than the line of additivity of the partial specific volume. The random coil of the PVA–PEG–water system is considered to be expanded, and those of the PVP–PEG–water and Dex–PEG–water systems are considered to be contracted.

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