Cloud-Point Measurements for Salt + Poly(ethylene glycol) + Water Systems by Viscometry and Laser Beam Scattering Methods

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ABSTRACT: The phase separation of salt + poly(ethylene glycol) + water systems was studied by cloud-point measurements using viscometry and laser beam scattering methods. The Flory–Huggins model was applied to determinate the condition for salt-induced liquid–liquid phase separation in the system. A temperature- and concentration-dependent interaction parameter was employed to fit the phase diagrams for the systems. The temperature and concentration functionality of the interaction parameter was determined and used to predict cloud-point curves for the systems. The cloud-point curves were found to be in quantitative agreement with experimental data. Also, the effect of various salts on the measured cloud points was studied. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1983–1990, 2003

Key words: light scattering; phase separation; viscosity

INTRODUCTION

Despite their importance in chemical technology (e.g., pharmaceuticals, detergents, food additives, cosmetics, textiles), few fundamental studies have been reported on the thermodynamic properties of water-soluble polymers.[1] Qian et al.[2,3] discussed mathematical modeling of polymer solutions, which display unusual phase diagrams. In recent years these polymers have received increased attention because of their use in two-phase aqueous systems for separation of biomolecular mixtures.[1] A salt–polymer aqueous two-phase system has potential use as separation media for liquid–liquid extraction of biological molecules.[4] Aqueous polymer two-phase systems are formed in water solutions and the aqueous phase systems are very favorable toward biological materials. The two-phase systems are formed with poly(ethylene glycol) (PEG) and dextran, or with PEG and salt.

Poly(ethylene glycol) is largely used as an additive to control the viscosity of paint, as an additive in the production of paper,[5] as a head group in nonionic surfactants, and to cover surfaces to prevent other polymers (e.g., proteins) from binding to the surface.[6] It has also been used since the mid-1950s for preparation of two-phase aqueous systems.[6] Recent developments within polymer and colloid research have been used for separation of biological macromolecules such as peptides and proteins.

Cloud-point measurements have been used to investigate the phase behavior of aqueous PEG solutions. It has been reported that the addition of salt and other additives affects the thermodynamic properties such as cloud point and theta temperature of aqueous PEG solutions.[7–11]

The cloud point of aqueous polymer solutions was measured by different physical techniques. To understand the cloud-point phenomenon, turbidimetry,[12–14] neutron scattering,[15] microcalorimetric study,[16] and low-angle light scattering measurements[17] have been used. The complete phase diagram for the PEG–water system was first determined by Sakei and coworkers.[6] For polymer–solvent mixtures Patterson and coworkers[18,19] reported measurements on solutions exhibiting phase separation. Densities of PEG + water systems were measured by Tawfic et al.[20] and Eliassi et al.[21] Viscosities of PEG/salt/water systems were determined by a number of researchers.[22–24]

PEG-based aqueous two-phase systems are formed when aqueous solutions of high molecular weight PEG are salted-out by specific aqueous salt solutions, providing two immiscible aqueous phases. Perhaps the most extreme effects are obtained if a salt such as potassium phosphate is added to the PEG–water system.[25] For this type of systems two phases already occur at room temperature. It seems that there is repulsion between the PEG molecules and the ions and this causes a phase separation into two phases in the
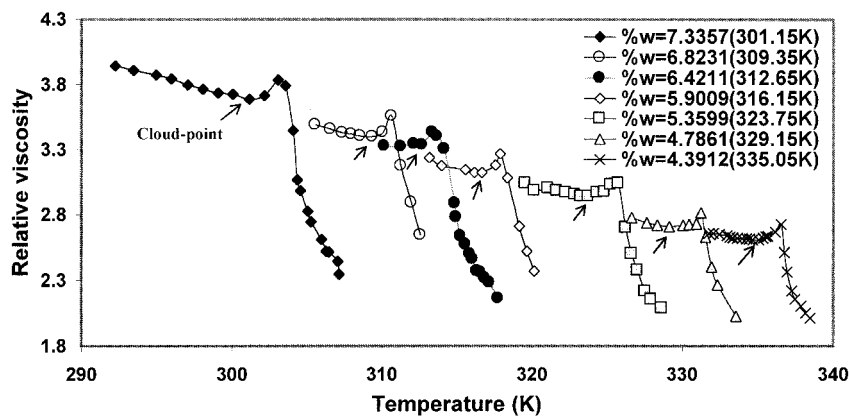
Figure 1 Effect of K_3PO_4 on viscosity of PEG15,000 + K_3PO_4 + water system [$m_{(PEG)}/m_{(water)} = 0.0712$]. The marks are experimental points and solid lines are drawn to show the variations.

same way as the addition of a second polymer (e.g., dextran) would do.[25]

Molecular mass and hydrophobicity of polymer, salt selection, salt and PEG system compositions, pH, temperature, and distance from the critical point are variables that affect aqueous two-phase systems.

Measurements of dilute solution viscosity have been widely used for routinely determining molecular mass.[26] In this work salt + PEG + water systems were studied by viscometry and laser beam scattering methods. The results of measurements in this work indicated that use of both methods to this new application (i.e. cloud-point measurements) is quite successful. The effect of various salts on cloud-point temperature of these systems was investigated.

EXPERIMENTAL

Materials and instruments

The polymers, PEG10,000 and PEG15,000, and the salts, KH_2PO_4, K_2HPO_4, Na_2HPO_4 and NaH_2PO_4, were all provided by Merck (Darmstadt, Germany) and K_3PO_4 was provided by Riedel-de Haën (Seelze,

Germany). The materials were dried at different temperatures (e.g., NaH_2PO_4 at 150°C). Double-distilled water was used for making the solutions, which were made by mass. Weighing of these samples was done with an analytical balance Bosch, with an accuracy of 0.1 mg. In making up the solutions, the relative weight of two components remained constant and the weight of the third component was changed. The viscometry measurements were done by Ubbelohde viscometer (Model Las 1156), equipped with a water bath and a thermostat to control the temperature with accuracy of 0.1°C. A chronometer measured the time of flow of solutions through the U-tube of the viscometer. The relative viscosity of solutions of salt + PEG + water was measured in the temperature range 25 to 65°C. On variation of temperature and by visual inspection of solutions the cloud points were observed. The viscometric measurement results were plotted versus temperature. The plots exhibited shallow minima in the viscosity at the cloud-point temperature.

A laser particle counter (Model PC-2000; Spectrex Corporation, Redwood City, CA) was used to study the scattering of laser beam on formation of particles
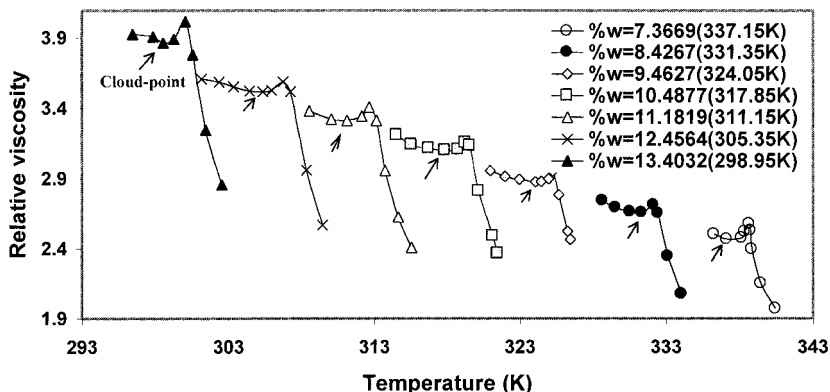

Figure 2 Effect of KH_2PO_4 on viscosity of PEG15,000 + KH_2PO_4 + water system [$m_{(PEG)}/m_{(water)} = 0.0712$]. The marks are experimental points and solid lines are drawn to show the variations.

Figure 3 Effect of NaH_2PO_4 on viscosity of PEG15,000 + NaH_2PO_4 + water system [$m_{(PEG)}/m_{(water)}$ = 0.0712]. The marks are experimental points and solid lines are drawn to show the variations.
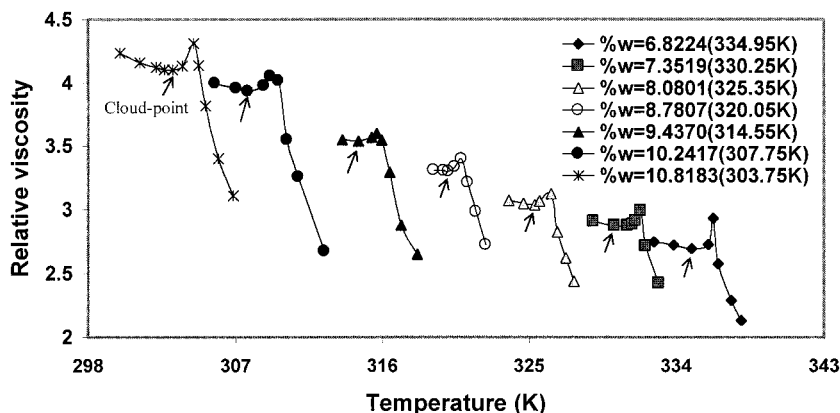
of the new phase. The laser particle counter has for its basic light source a laser diode (wavelength 670.8 nm). The required time for determining the number of particles was 15 s. The temperature of the water bath was changed and controlled by a thermostat (Fisher Scientific, Pittsburgh, PA) at an appropriate rate to maintain the required temperature at the flow cell. At each temperature, the output of the apparatus was sent to a PC, after which a printer recorded the number of particles per cubic centimeter. The temperature of the solution was recorded at the entrance of the cell by a thermocouple. In laser beam scattering a sharp change in the intensity of the scattered laser beam was observed to coincide with the measured cloud points by both viscometric and visual inspection.

RESULTS AND DISCUSSION

Obtained results for viscosity change of electrolytic polymer solutions are presented in Figures 1 to 3.

According to these figures, on increasing the temperature of the solution, the viscosity of solution decreased. The cloud points were determined at the minimum of the curves obtained on plotting the measured viscosities versus variation of temperature (see Figs. 1 to 3). The recorded temperature was the cloud point of the mixture. As seen from the figures, the viscosity after passing through a minimum begins to increase and then decrease again, but more intensively. This phenomenon can be explained by the fact that at higher temperature the molecular motions overcome the molecular interactions and then, as expected, the viscosity decreases. However, at the cloud point the number of particles of the new phase suddenly increases (see Fig. 4), and this causes an increase in the viscosity, which is dominant over the viscosity decrease because of the temperature increase.

A part of the experimental results of laser beam measurements for the salt KH_2PO_4 is shown in Figure 4, which shows the change in number of particles at
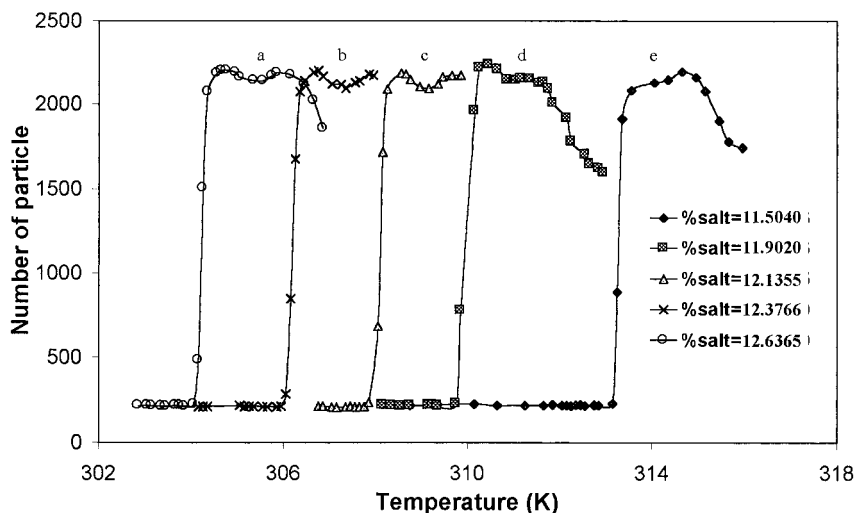

Figure 4 Effect of KH_2PO_4 on number of particle created in PEG10,000 + KH_2PO_4 + water system [$m_{(PEG)}/m_{(water)}$ = 0.1111]. The marks are experimental points and solid lines are drawn to show the variations.

TABLE I
Measured Cloud Points by Viscometry (*) and Laser Beam Scattering (**) Methods for PEG + Salt + Water Systems

	PEG15,000 + K_3PO_4 + water system [$m_{(PEG)}/m_{(water)}$ = 0.0712]*						
ϕ_{salt}	0.0269	0.0248	0.0240	0.0231	0.0213	0.0200	0.0188
$T(K)$	301.15	309.35	312.65	316.15	323.75	329.15	335.05
	PEG15,000 + KH_2PO_4 + water system [$m_{(PEG)}/m_{(water)}$ = 0.0712]*						
ϕ_{salt}	0.0483	0.0449	0.0422	0.0394	0.0371	0.0347	0.0328
$T(K)$	298.55	305.35	311.15	317.85	324.05	331.35	337.15
	PEG15,000 + NaH_2PO_4 + water system [$m_{(PEG)}/m_{(water)}$ = 0.0712]*						
ϕ_{salt}	0.0505	0.0483	0.0448	0.0422	0.0402	0.0383	0.0367
$T(K)$	303.75	307.75	314.55	320.05	325.35	330.25	334.95
	PEG10,000 + NaH_2PO_4 + water system [$m_{(PEG)}/m_{(water)}$ = 0.1113]						
ϕ_{salt}	0.0425	0.0477	0.0532	0.0561	0.0583		
$T(K)$*	—	321.15	312.11	—	302.65		
$T(K)$**	327.15	320.45	311.45	306.55	302.55		
	PEG10,000 + Na_2HPO_4 + water system [$m_{(PEG)}/m_{(water)}$ = 0.1114]**						
ϕ_{salt}	0.0247	0.0253	0.0287	0.0305			
$T(K)$	327.15	325.55	316.45	310.65			
	PEG10,000 + KH_2PO_4 + water system [$m_{(PEG)}/m_{(water)}$ = 0.1111]						
ϕ_{salt}	0.0515	0.0535	0.0547	0.0559	0.0572		
$T(K)$*	313.95	—	307.85	—	304.25		
$T(K)$**	313.15	309.75	307.85	305.95	304.05		
	PEG10,000 + K_2HPO_4 + water system [$m_{(PEG)}/m_{(water)}$ = 0.1117]**						
ϕ_{salt}	0.0220	0.0242	0.0261	0.0276	0.0288		
$T(K)$	323.55	317.15	311.45	306.65	303.15		

various temperatures for four different solutions. According to Figure 4(a), in the temperature range 302.00 to 303.85 K, the number of particles remains constant, but at 304.05 K, a sharp increase is observed which is attributed to the appearance of the first particles of the new phase. Therefore the 304.05 K is recorded as the cloud point of the mixture. As seen from these figures, the number of particles after passing through a maximum then begins to decrease.

The phase separation was also observed by visual inspection of the mixture where two clear transparent phases were seen in the mixture.

The cloud points for aqueous solutions of PEG10,000 and PEG15,000 with inorganic salt at various concentrations were measured. The results obtained by viscometric and laser beam scattering methods are given in Table I. Reproducibility of the results was excellent and the accuracy of the cloud points was estimated to be better than ±0.1°C in both methods. The results indicated 0.1 to 1.0°C differences between the measured cloud points using the viscometry method and visual inspection and 0.7–1.5°C differences between the measured cloud points using the particle counter method and visual inspection.

The variations of cloud-point temperature measured by the viscometric method versus weight fraction of salt are shown in Figure 5. As seen from this

figure, there is a linear variation of cloud points on variation of salt weight fractions and this will be used to model thermodynamic properties of these systems. The modeling of the experimental results is discussed in the next sections.

In Figure 6 variations of cloud point measured by the laser method versus weight fraction of salts are shown.

It can be seen from Figures 5 and 6 that the variation of the cloud points versus concentration of the salt is linear, and that the higher the cation size, the more efficacious is the decrease of the cloud point. On the other hand, these results show that sodium ion is more effective than potassium on decreasing the cloud point of the solution. Thus it can be concluded that an increase in the size of the cation can lower the cloud point of aqueous PEG + salt solutions. As seen in Figure 5, the charge magnitude effect of anions (A) is in the following order: $A^{3-} > A^{2-} > A^{-}$.

In Figure 7 the effect of molecular weight of PEG on the cloud point of aqueous solutions of PEG + NaH_2PO_4 can be seen. According to this figure, the cloud point of the solution decreases by increasing the molecular weight of PEG.

The results obtained in this work substantiate the conclusion by other investigators that clouding may be induced either by adding substances that are more
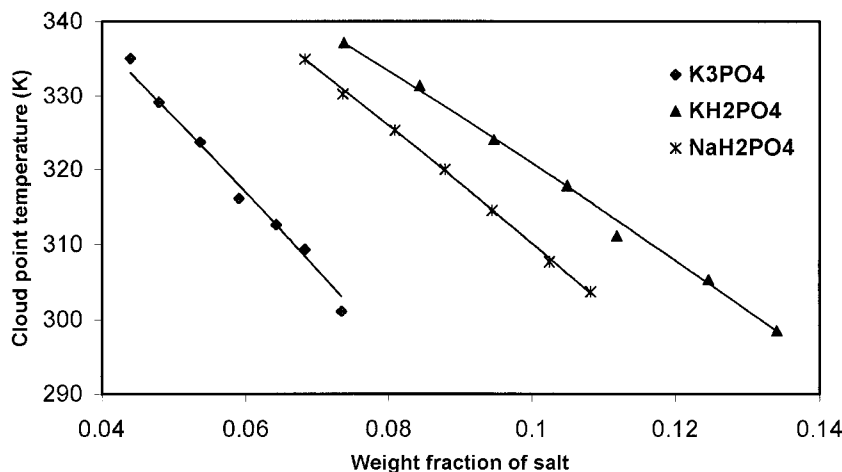
Figure 5 Effect of salt type on PEG15000 + salt + water system [$m_{(PEG)}/m_{(water)}$ = 0.0712] as obtained in the viscometry method. The marks are experimental points and solid lines are calculated by eqs. (15) and (16).

polar than water or by adding substances that are less polar than the polymer.[27]

FLORY–HUGGINS MODEL AND CORRELATING EQUATIONS

Flory–Huggins theory is particularly useful for describing solutions of polymers in liquid solvents and is a cornerstone of polymer–solution thermodynamics.[28] It is derived[29,30] by approaching the polymer solution as a lattice of sites, each of which is occupied by either a solvent molecule or a polymer segment.[28] The volume fractions represent the fraction of lattice sites occupied by each substance.[3] In the derivation of the theory, it is assumed that the solvent and the polymer segments occupy the same volume and they can be interchanged with no change in the lattice; that is, no volume change is allowed to occur upon mixing.[3] This

assumption has turned out to be the most restrictive feature of the theory.[3]

Binary mixtures

According to the Flory–Huggins theory the chemical potential of solvent (μ_1) in a binary mixture is given by the following expressions[31,32]:

$$\Delta\mu_1 = RT(\ln \phi_1 + (1 - 1/r)\phi_2 + \chi(T, \phi_2)\phi_2^2) \quad (1)$$

where μ_i and ϕ_i are the chemical potential and volume fraction of component i, respectively; r is segment number of polymer and is equal to polymer molar volume divided by solvent molar volume. The interaction between solvent molecules and segments of the polymer is characterized by the parameter $\chi(T, \phi_2)$.
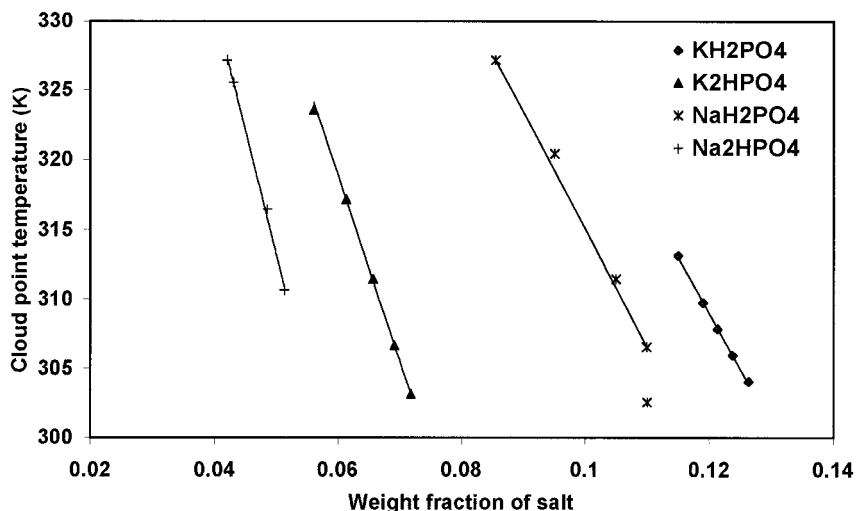

Figure 6 Effect of salt type on PEG10000 + salt + water system as obtained in the laser beam scattering method [$m_{(PEG)}/m_{(water)}$ = 0.1111]. The marks are experimental points and solid lines are calculated by eqs. (15) and (16).
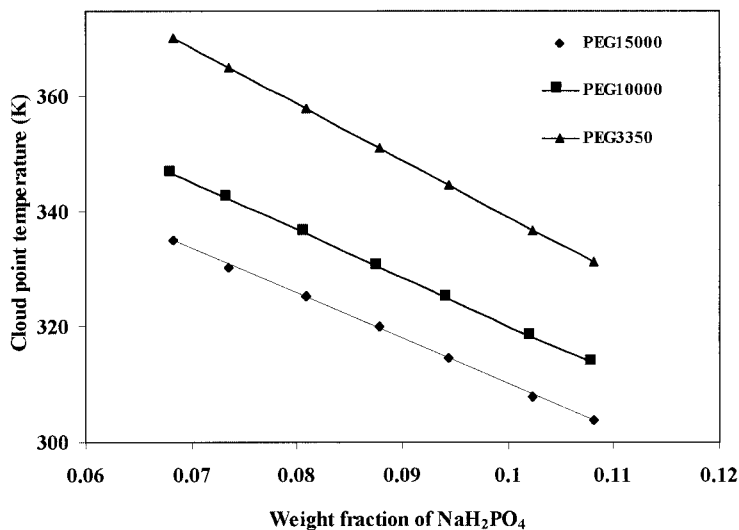
Figure 7 Effect of molecular weight of PEG on PEG + NaH_2PO_4 + water systems [$m_{(PEG)}/m_{(water)}$ = 0.0712].

This parameter has a very important role in polymer solutions theory. In fact, one of the problems in the Flory–Huggins theory is the exact determination of χ. Relative vapor pressure and osmotic pressure measurements are examples of experimental methods for determination of χ.[33]

For the cloud-point temperatures we have following condition[3,19,34]:

$$\Delta\mu_1 = 0 \qquad (2)$$

Upon substitution of eq. (1) in eq. (2) we get

$$\ln\phi_1 + (1 - 1/r)\phi_2 + \chi(T, \phi_2)\phi_2^2 = 0 \qquad (3)$$

Equation (3) is valid in certain thermodynamic conditions at temperature (T) and volume fraction (ϕ_2), provided that a homogeneous polymer solution or mixture separates into two or more phases. Now, according to the approach of Qian and coworkers,[2,3] we assume that $\chi(T, \phi_2)$ is a function of concentration $B(\phi_2)$ and temperature $D(T)$:

$$\chi(T, \phi_2) = B(\phi_2)D(T) \qquad (4)$$

The proposed forms for $D(T)$ and $B(\phi_2)$ are

$$D(T) = d_0 + \frac{d_1}{T} + d_2\ln T \qquad (5)$$

$$B(\phi_2) = b_0 + b_1\phi_2 + b_2\phi_2^2 \qquad (6)$$

The proper relation between cloud-point temperature (T) and solution composition (ϕ_2) can create the expected types of phase diagram for polymer solution systems.

Ternary mixtures

The Flory–Huggins equation for a three-component mixture is given as[31,32,35]

$$\Delta\mu_1 = RT(\ln\phi_1 + (1 - 1/r_2)\phi_2 + (1 - 1/r_3)\phi_3$$
$$+ \chi_{12}\phi_2(1 - \phi_1) + \chi_{13}\phi_3(1 - \phi_1) - \chi_{23}\phi_2\phi_3/r_2) \qquad (7)$$

TABLE II
Calculated Parameters for PEG + Salt + Water Systems Measured by Viscometry (*)
and Laser Beam Scattering Methods (**)

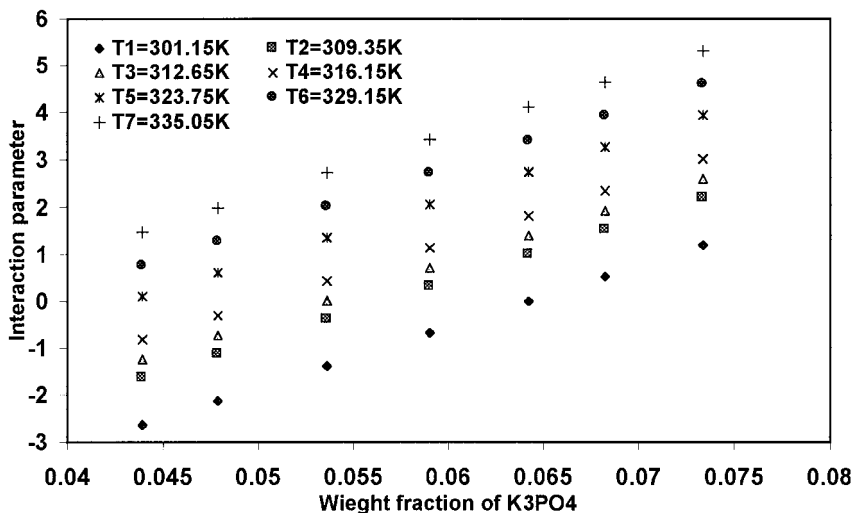| PEG	Salt	$m_{(PEG)}/m_{(water)}$	Adjustable parameters		
			c_0	c_1	c_2
PEG15,000*	NaH_2PO_4	0.0712	−97.3354	0.2074	331.0090
	KH_2PO_4	0.0712	−104.3050	0.2286	329.8464
	K_3PO_4	0.0712	−64.2748	0.1212	338.1875
PEG10,000**	NaH_2PO_4	0.1113	−102.3970	0.1889	330.2654
	Na_2HPO_4	0.1114	−69.5862	0.1009	338.5805
	KH_2PO_4	0.1111	−99.1833	0.1791	338.1203
	K_2HPO_4	0.1117	−64.7037	0.0896	338.1203

Figure 8 The variation of χ_{12}^{*} versus weight fraction of salt at constant temperatures obtained by the viscometry method.

where ϕ_1, ϕ_2, and ϕ_3 are the volume fractions of solvent, salt, and polymer, respectively. Also, χ_{12}, χ_{13}, and χ_{23} are the interaction parameters between the components in the mixture, and r_2 and r_3 are the segment numbers defined for salt and polymer components, respectively.

To represent eq. (7) in a simple form we introduce ϕ_2^{*} as the sum of salt and polymer volume fractions, represented as[32]

$$\phi_2^{*} = \phi_2 + \phi_3 \qquad (8)$$

Also, r_2^{*} is introduced as[32]

$$r_2^{*} = x_2^{*}r_2 + x_3^{*}r_3 \qquad (9)$$

where x_2^{*} and x_3^{*} are defined as the mole fractions of salt and polymer in solvent, respectively:

$$x_2^{*} = \frac{x_2}{x_2 + x_3} \qquad (10a)$$

$$x_3^{*} = \frac{x_3}{x_2 + x_3} \qquad (10b)$$

By substituting eqs. (8)–(10a,b) in eq. (7) we get

$$\Delta\mu_1 = RT(\ln \phi_1 + (1 - 1/r_2^{*})\phi_2^{*} + \chi_{12}^{*}(T, \phi_2^{*})\phi_2^{*2}) \qquad (11)$$

χ_{12}^{*} is introduced as[32]

$$\chi_{12}^{*} = ((\chi_{12}\phi_2 + \chi_{13}\phi_3)(1 - \phi_1)$$
$$- \chi_{23}\phi_2\phi_3/r_2)/(1 - \phi_1)^2 \qquad (12)$$

By use of eq. (11) in the cloud-point condition represented by eq. (2), the following equation will be obtained:

$$\ln \phi_1 + (1 - 1/r_2^{*})\phi_2^{*} + \chi_{12}^{*}(T, \phi_2^{*})\phi_2^{*2} = 0 \qquad (13)$$

This equation can be used for cloud-point calculations. However, finding a proper functionality of temperature (T) and volume fraction (ϕ_2^{*}) for the interaction parameter $\chi_{12}^{*}(T, \phi_2^{*})$ is an important task.[36]

Fortunately, our cloud-point results indicated that the simple functionality presented by eq. (14) is the most proper one to fit in eq. (13):

$$\chi_{12}^{*} = c_0 + c_1T + c_2\phi_2^{*} \qquad (14)$$

The values of coefficients c_0, c_1, and c_2 are reported in Table II. In Figure 8 the variation of χ_{12}^{*} versus weight fraction of salt at constant temperatures is presented. According to Figure 8, for three-component systems, when the mass ratio of polymer to water is constant, then on increasing the amount of K_3PO_4, the χ values will increase. From this figure, it is obvious that at higher temperatures these changes occur at higher values of χ. The same results can be obtained for the other six systems studied in this work. It is worth noting that the χ parameter is an increasing function of temperature at the vicinity of the cloud points of the systems.

CONCLUSIONS

Cloud-point data for salt + poly(ethylene glycol) + water systems were obtained by viscometry and laser beam scattering methods. The experimental results were used in the Flory–Huggins system of equations, the coefficients of the interaction parameter were evaluated, and the cloud-point curves were produced for these systems. The effect of various salts on the cloud-point temperature was investigated.

References

1. Haynes, C. A.; Beynon, R. A.; King, R. S.; Blanch, H. W.; Prausnitz, J. M. J Phys Chem 1989, 93, 5612.
2. Qian, C.; Mumby, S. J.; Eichinger, B. E. J Polym Sci Part B: Polym Phys 1991, 29, 635.
3. Qian, C.; Mumby, S. J.; Eichinger, B. E. Macromolecules 1991, 24, 1655.
4. Toshiaki, H.; Prausnitz, J. M. J Appl Polym Sci 1998, 68, 2007.
5. Zalipsky, S.; Harris, J. M. Introduction to Chemistry and Biological Applications of Poly(ethylene glycol); University of Alabama Press: Huntsville, 1997.
6. Sakei, S.; Kuwahara, N.; Nakata, M.; Kaneko, M. Polymer 1976, 17, 685.
7. Boucher, E. A.; Hines, P. M. J Polym Sci Part B: Polym Phys 1976, 14, 2241.
8. Boucher, E. A.; Hines, M. J Polym Sci Part B: Poly Phys 1978, 16, 501.
9. Ataman, M. Colloid Polym Sci 1987, 265, 19.
10. Ataman, M.; Boucher, E. A. J Polym Sci Part B: Polym Phys 1982, 20, 1585.
11. Ataman, M. J Macromol Sci Chem 1987, A24, 967.
12. Friedrich, F.; Schwarzwalder, C.; Riemann, R. E. Polymer 1996, 37, 2499.
13. Boutris, C.; Chatzi, E. G.; Kiparissides, C. Polymer 1997, 38, 2567.
14. Jarm, V.; Sertic, S.; Segudvic, N. J Appl Polym Sci 1995, 58, 1973.
15. Thiyagarajan, P.; Chaiko, D. J.; Hjelm, R. P. Macromolecules 1995, 28, 7730.
16. Howard, G.; Tirrell, S. D. A. J Phys Chem 1990, 94, 4352.
17. Rebelo, L. P.; Wavhook, W. A. J Polym Sci Part B: Polym Phys 1993, 31, 895.
18. Siow, K. S.; Delmas, G.; Patterson, D. Macromolecules 1972, 5, 29.
19. Zeman, L.; Patterson, L. D. J Phys Chem 1972, 76, 1214.
20. Tawfic, W. Y.; Teja, A. S. Chem Eng Sci 1989, 44, 921.
21. Eliassi, A.; Modarress, H.; Mansoori, G. A. J Chem Eng Data 1998, 43, 719.
22. Tello, P. G.; Gomacho, F.; Blazquez, G. J Chem Eng Data 1994, 39, 611.
23. Muller, E. A. J Chem Eng Data 1991, 36, 214.
24. Mei, L. H.; Lin, D. Q.; Zhu, Z. Q.; Han, Z. X. J Chem Eng Data 1995, 40, 1168.
25. Albertson, P. A. Partition of Cell Particles and Macromolecules, 2nd ed.; Almqvist & Wiksell: Stockholm, 1971.
26. Malcolm, P. S. Polymer Chemistry: An Introduction; University of Hartford Press: Hartford, CT, 1975.
27. Johansson, H. O.; Karlstrom, G.; Tjerneld, F. Macromolecules 1993, 26, 4478.
28. Prausnitz, J. M.; Lichtenthaler, R. L.; Azevedo, E. G. Molecular Thermodynamics of Fluid-Phase Equilibria; Prentice Hall: Englewood Cliffs, NJ, 1999.
29. Hilderbrand, J. H.; Prausnitz, J. M.; Scott, R. L. Regular and Related Solutions; Van Nostrand Reinhold: New York, 1970.
30. Albertson, P. A. Partitions of Cells and Macromolecules; Wiley: New York, 1985.
31. Flory, P. J. Principles of Polymer Chemistry; Cornell University Press: Ithaca, NY, 1953.
32. Eliassi, A.; Modarress, H. Eur Polym J 2001, 37, 1487.
33. Tager, A.; Sobolev, D.; Babrov, N. Physical Chemistry of Polymers; Mir Publishers: Moscow, 1972.
34. Bae, Y. C.; Shim, J. J.; Soane, D. S.; Prausnitz, J. M. J Appl Polym Sci 1993, 47, 1193.
35. Sargantanis, I. G.; Karim, M. N. Ind Eng Chem Res 1997, 36, 204.
36. Fischer, V.; Borchard, W.; Karas, M. J Phys Chem 1996, 100, 15992.