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Short communication

Interfacial tension of aqueous two-phase systems containing poly(ethylene glycol) and dipotassium hydrogenphosphate

K. Mishima*, K. Matsuyama, M. Ezawa, Y. Taruta, S. Takarabe, M. Nagatani

Department of Chemical Engineering, Faculty of Engineering, Fukuoka University, Nanakuma Jonanku, Fukuoka 814-80, Japan

Abstract

Liquid–liquid equilibrium (LLE) compositions and interfacial tensions of the aqueous two-phase system containing poly(ethylene glycol) (PEG 4000, average $M_r=3500$; PEG 6000, average $M_r=7500$; and PEG 20 000, average $M_r=20\ 000$) and dipotassium hydrogenphosphate were experimentally determined by using a shaking flask method and a drop volume method at 288.15, 298.15 and 308.15 K, respectively. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Aqueous two-phase systems; Interfacial tension; Poly(ethylene glycol); Dipotassium hydrogenphosphate

1. Introduction

Despite the fact that aqueous two-phase partitioning has been used extensively for the separation of biological materials in the laboratory [1,2], there is no accurate way to predict the physicochemical properties, such as interfacial tension and partitioning of polymers and biomolecules in these systems because of lack of data. Interfacial tension is important for the design of extraction equipment. In order to aid in rational equipment design and optimization of large-scale purification processes in bio-separation industry, a better understanding of phase equilibrium compositions and interfacial tensions should be investigated for the aqueous two-phase system needed. Liquid–liquid equilibrium (LLE) compositions and interfacial tensions should be measured systematically at the same feed composi-

tions, because the interfacial tension of the aqueous two-phase system changes remarkably with the concentrations of polymer and electrolyte.

Therefore experimental LLE compositions and interfacial tensions of the aqueous two-phase systems containing two kinds of polymers, such as poly(ethylene glycol) (PEG) and dextran, have been reported [3]. Recently, the equilibrium phase compositions were explored for aqueous PEG and electrolyte mixtures [4–9]. However, interfacial tension data of aqueous two-phase systems containing electrolyte are relatively scarce. Except for this work, there have been few published interfacial tension data, or descriptions of the factors that influence interfacial tension [10–12].

In this work, the effects of the molecular mass of polymer on liquid–liquid equilibrium (LLE) compositions and interfacial tensions were reported in the PEG 4000 (1)– K_2HPO_4 (2)–water (3), PEG 6000 (1)– K_2HPO_4 (2)–water (3) and PEG 20 000 (1)– K_2HPO_4 (2)–water (3) systems at 298.15 K. Furthermore, the effect of temperature on the interfacial

*Corresponding author

tension of the PEG 6000 (1)–K₂HPO₄ (2)–water (3) system is discussed.

2. Experimental

2.1. Materials

Poly(ethylene glycol) (PEG 4000, average M_r = 3500; PEG 6000, average M_r = 7500; and PEG 20 000, average M_r = 20 000) and dipotassium hydrogenphosphate (K₂HPO₄) were purchased from Wako Pure Chemical Ind. (Osaka, Japan). Their purities were more than 95 and 99% for PEG and K₂HPO₄, respectively. PEG was purified under vacuum at room temperature for 1 day. K₂HPO₄ was dried for 5 h at 383.15 K. Water was purified with an ultra-pure water apparatus (Milli-Q Labo, Nihon Millipore, Tokyo, Japan).

2.2. LLE

Binodal curves were determined by observation of the cloud point. In brief, aqueous PEG solutions were prepared by weight. The sample in the cell was stirred using an agitator. Cloud points were determined optically in a water bath maintained at the desired temperature. The temperature control accuracy of the system was 0.05 K. A He–Ne laser light was passed through the cell, and the intensity of transmitted light was monitored with a photosensor. Near the cloud point, the aqueous K₂HPO₄ solution was carefully charged. The intensity of the transmitted light decreased sharply when the charging amount of aqueous K₂HPO₄ solution passed through the cloud point. In this way, the cloud point fractions were measured.

Details of the measuring procedure of LLE compositions were described in our previous papers [7,8]. A certain amount of aqueous solution containing PEG and/or K₂HPO₄ was placed in an equilibrium cell, whose volume was about 100 ml. The cells were shaken for 10 min with a mechanical shaker and allowed to stand for more than 48 h in a water bath maintained at 298.15 K. After the separation of the two phases, the concentrations of PEG in the top (I) and bottom (II) phases were determined by high-performance liquid chromatog-

raphy (HPLC-8000, Tosoh Co., Tokyo, Japan) and using a total organic carbon analyzer (TOC-10B, Shimadzu Co., Kyoto, Japan), respectively. The concentrations of K₂HPO₄ in both phases were determined by titration with hydrochloric acid. Methyl orange was used as indicator. Densities of each phase were measured by a pycnometer.

2.3. Interfacial tension

The interfacial tension of these systems was determined by a drop volume method [13] at 288.15, 298.15 and 308.15 K. Some burettes having capillaries with various outer diameters were used, because a remarkable change of the interfacial tension in the aqueous two-phase system occurred with the LLE composition change. In general, the interfacial tensions depend extensively on the system temperature. A stoppered burette cell, whose volume was about 50 ml, was immersed in a water-bath maintained at the desired temperature. Top and bottom phase solutions obtained from the above-mentioned LLE experiments were separated and added to an interfacial tension cell and a burette, respectively. A liquid drop consisting of the bottom phase compositions was carefully formed downwards at the tip of capillary with an outer diameter which is wettable with the liquid contained in a burette. It took more than 10 min to form a drop. Interfacial tension was determined from the number and volume of drops fallen downward by utilizing liquid density of top and bottom phase solutions. In our previous work [7,8], the reproducibility of the experimental LLE composition data was estimated within $\pm 3\%$. Interfacial tension of the aqueous two-phase system is strongly dependent upon LLE compositions. The overall error, including that in TLL and other possible systematic errors, is 3%.

3. Results and discussion

To confirm the reliability of experimental equilibrium compositions, binodal curves of the PEG 4000 (1)–K₂HPO₄ (2)–water (3) and PEG 20 000 (1)–K₂HPO₄ (2)–water(3) systems at 298.15 K are shown in Table 1 and Fig. 1, with the values of the PEG 6000 (1)–K₂HPO₄ (2)–water (3) system re-

Table 1

Binodal curves for PEG 4000 (1)–K₂HPO₄ (2)–water (3) and PEG 20 000 (1)–K₂HOP₄ (2)–water (3) systems at 298.15 K

| PEG 4000 | | | PEG 20 000 | | |
|----------------|----------------|----------------|----------------|----------------|----------------|
| W_1^a (wt.%) | W_2^a (wt.%) | W_3^a (wt.%) | W_1^a (wt.%) | W_2^a (wt.%) | W_3^a (wt.%) |
| 36.0 | 2.2 | 61.8 | 33.1 | 2.6 | 64.3 |
| 31.9 | 2.8 | 65.3 | 30.0 | 3.0 | 67.1 |
| 28.5 | 3.4 | 68.1 | 27.0 | 3.4 | 69.9 |
| 25.7 | 3.9 | 70.4 | 24.3 | 3.9 | 71.8 |
| 20.8 | 5.2 | 74.0 | 22.2 | 4.0 | 73.7 |
| 17.0 | 6.1 | 76.9 | 20.2 | 4.4 | 75.4 |
| 13.9 | 7.2 | 78.9 | 16.4 | 4.8 | 78.8 |
| 10.1 | 8.7 | 81.2 | 15.2 | 5.1 | 79.7 |
| 7.9 | 9.5 | 82.6 | 14.0 | 5.5 | 80.5 |
| 6.5 | 10.1 | 83.4 | 12.0 | 6.0 | 82.1 |
| 5.8 | 10.6 | 84.0 | 10.5 | 6.3 | 83.2 |
| 4.7 | 11.0 | 84.3 | 9.2 | 7.0 | 84.1 |
| 0.8 | 15.0 | 84.2 | 8.3 | 6.9 | 84.8 |
| 0.3 | 21.8 | 77.9 | 7.6 | 7.0 | 85.4 |
| | | | 6.9 | 7.3 | 85.9 |
| | | | 6.6 | 7.3 | 86.1 |

^a W_i is the equilibrium mass fraction (%) of component i .

ported in our previous paper [8]. It was found that the two-phase area is expanded with an increase in the molecular mass of polymer, as was the case of the PEG (1)–(NH₄)₂SO₄ (2)–water (3) system

reported by Voros et al. [6]. Equilibrium compositions of these systems are shown in Figs. 2 and 3 and Table 2. An increase of the molecular mass of PEG will cause an increase of polymer concentration in the top phase and a decrease in the bottom phase,

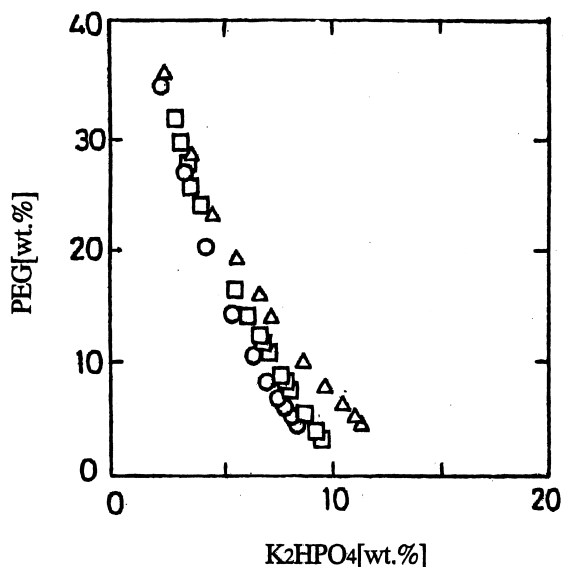


Fig. 1. Binodal curves for the PEG (1)–K₂HPO₄ (2)–water (3) system at 298.15 K. (△) PEG 4000; (□) PEG 6000 [8]; (○) PEG 20 000.

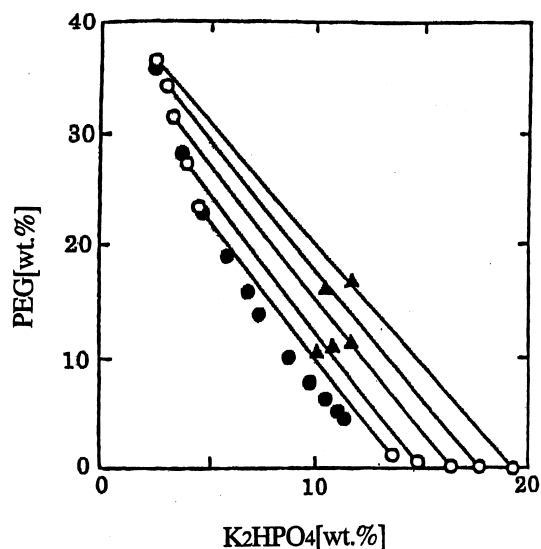


Fig. 2. Phase equilibrium compositions for the PEG 4000 (1)–K₂HPO₄ (2)–water (3) system at 298.15 K. (●) Binodal; (○) tie-line; (▲) feed.

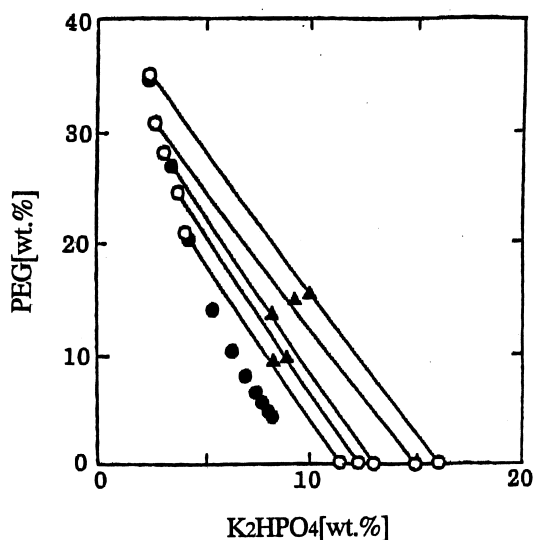


Fig. 3. Phase equilibrium compositions for the PEG 20 000 (1)–K₂HPO₄ (2)–water (3) system at 298.15 K. (●) Binodal; (○) tie-line; (▲) feed.

respectively. These results agree with those reported by Voros et al. [6].

Interfacial tensions, σ , of the PEG 4000 (1)–K₂HPO₄ (2)–water (3), PEG 6000 (1)–K₂HPO₄ (2)–water (3) and PEG 20 000 (1)–K₂HPO₄ (2)–water (3) systems measured at 298.15 K are shown in Table 3 and Fig. 4 along with the literature values of the PEG 4000 (1)–K₂HPO₄ (2)–water (3) system reported by Wu et al. [10]. Similar results were obtained in the case of PEG 4000 (1)–K₂HPO₄

Table 2

Liquid–liquid equilibria for the PEG (1)–K₂HOP₄ (2)–water (3) system at 298.15 K

| System | Tie-line no. | W^F (wt.%) | | | W^{TOP} (wt.%) | | | W^{BOT} (wt.%) | | |
|-----------------------|--------------|--------------|------|------|------------------|-----|------|------------------|------|------|
| | | (1) | (2) | (3) | (1) | (2) | (3) | (1) | (2) | (3) |
| System A ^a | 1 | 10.6 | 10.1 | 79.4 | 23.2 | 4.5 | 72.3 | 1.2 | 13.5 | 85.3 |
| | 2 | 11.1 | 10.8 | 73.1 | 27.2 | 3.2 | 65.4 | 0.3 | 16.2 | 83.5 |
| | 3 | 11.4 | 11.6 | 76.9 | 31.4 | 3.2 | 65.4 | 0.1 | 17.6 | 82.3 |
| | 4 | 16.1 | 10.5 | 73.4 | 34.0 | 2.9 | 63.1 | 0.1 | 17.6 | 82.3 |
| | 5 | 16.8 | 11.7 | 71.5 | 36.4 | 2.4 | 61.2 | 0.04 | 19.2 | 80.7 |
| System B ^b | 1 | 9.5 | 8.3 | 82.3 | 20.8 | 4.0 | 75.2 | 0.6 | 11.3 | 88.1 |
| | 2 | 9.7 | 8.9 | 81.4 | 22.2 | 3.6 | 74.1 | 0.2 | 12.2 | 87.6 |
| | 3 | 13.6 | 8.2 | 78.2 | 25.9 | 3.0 | 71.1 | 0.1 | 12.9 | 86.9 |
| | 4 | 14.8 | 9.3 | 75.9 | 30.5 | 2.6 | 34.0 | 0.06 | 14.8 | 85.1 |
| | 5 | 15.4 | 10.0 | 74.6 | 35.1 | 2.3 | 62.6 | 0.04 | 16.0 | 84.0 |

^aSystem A: PEG 4000 (1)–K₂HOP₄ (2)–water (3) system at 298.15 K.

^bSystem B: PEG 20 000 (1)–K₂HOP₄ (2)–water (3) system at 298.15 K.

Table 3

Interfacial tension of PEG (1)–K₂HOP₄ (2)–water (3) systems

| System | σ ($\times 10^4$ N m ⁻¹) | | | | |
|----------------|--|------|------|------|------|
| | Tie-line no.: | | | | |
| | 1 | 2 | 3 | 4 | 5 |
| A ^a | 1.15 | 1.77 | 2.75 | 3.71 | 4.78 |
| B ^b | 0.98 | 1.85 | 3.38 | 4.71 | 6.45 |
| C ^c | 1.70 | 2.24 | 3.98 | 7.59 | 12.6 |
| D ^d | — | 1.53 | 2.05 | 2.94 | 4.03 |
| E ^e | 1.49 | 3.39 | 4.32 | — | 9.03 |

^aPEG 4000 (1)–K₂HOP₄ (2)–water (3) system at 298.15 K.

^bPEG 6000 (1)–K₂HOP₄ (2)–water (3) system at 298.15 K.

^cPEG 20 000 (1)–K₂HOP₄ (2)–water (3) system at 298.15 K.

^dPEG 6000 (1)–K₂HOP₄ (2)–water (3) system at 288.15 K.

^ePEG 6000 (1)–K₂HOP₄ (2)–water (3) system at 308.15 K.

(2)–water (3) system. This demonstrates the reliability of our experimental method of interfacial tension. In these systems, interfacial tension increases with an increase in tie-line length (TLL) and molecular mass of PEG. TLL is defined as follows:

$$TLL = [(W_1^{TOP} - W_1^{BOT})^2 + (W_2^{TOP} - W_2^{BOT})^2]^{1/2} \quad (1)$$

where W_1 and W_2 are the equilibrium mass fractions (%) of PEG and K₂HPO₄, respectively. There is a linear relationship between $\log \sigma$ and $\log TLL$. Similar results were reported for the solutions containing two kinds of polymers, such as PEG and dextran [3,11]. However, the degree of effect of solute concentration of electrolyte on interfacial tension is

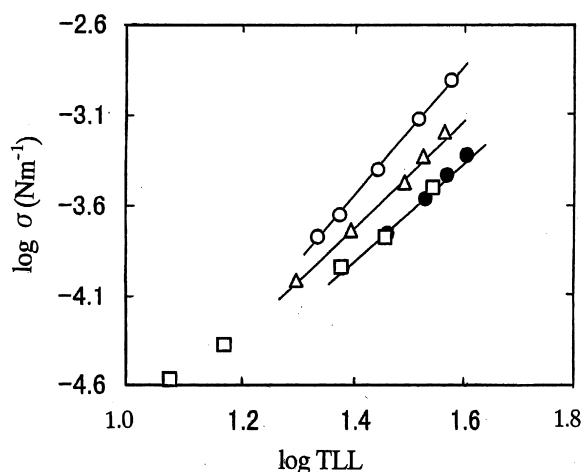


Fig. 4. Log–log plots of interfacial tension versus tie-line length (TLL) for PEG (1)–K₂HPO₄ (2)–water (3) system at 298.15 K. (●) PEG 4000; (□) PEG 4000 [10]; (△) PEG 6000; (○) PEG 20 000.

larger than that of the polymer. Furthermore, the effect of temperature on the interfacial tension of PEG 6000 (1)–K₂HPO₄ (2)–water (3) system is shown in Table 3 and Fig. 5. The same TLL gives

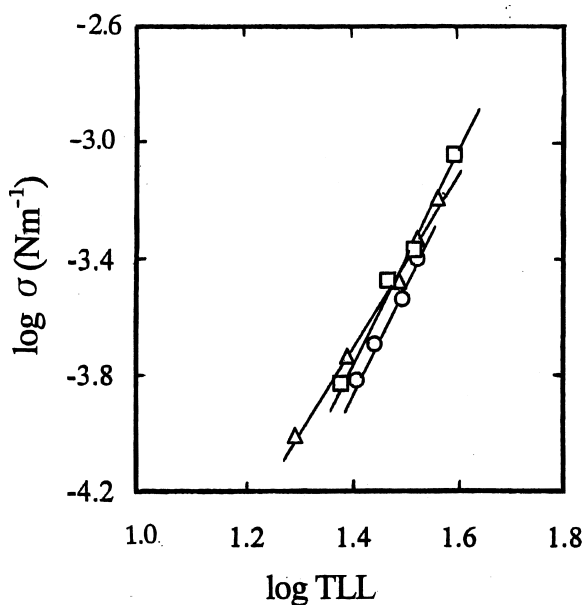


Fig. 5. Log–log plots of interfacial tension versus tie-line length (TLL) for PEG 6000 (1)–K₂HPO₄ (2)–water (3) system at 288.15, 298.15 and 308.15 K. (○) 288.15 K; (△) 298.15 K; (□) 308.15 K.

Table 4

Correlation results of interfacial tension versus TLL for PEG (1)–K₂HPO₄ (2)–water (3) systems with Eq. (2)

| System ^a | <i>a</i> (—) | <i>b</i> (—) | Dev. (%) ^b |
|---------------------|--------------|--------------|-----------------------|
| A | –7.738 | 2.746 | 3.4 |
| B | –7.906 | 3.001 | 4.0 |
| C | –8.613 | 3.623 | 2.0 |
| D | –8.833 | 3.558 | 2.6 |
| E | –8.775 | 3.589 | 5.1 |

^aSame as in Table 3.

$${}^b\text{Dev.} = \frac{1}{N} \sum_i \left(\frac{|\sigma_{i,\text{exp.}} - \sigma_{i,\text{calc.}}|}{\sigma_{i,\text{exp.}}} \right) \times 100$$

almost the same value of interfacial tension. Figs. 4 and 5 and Table 4 show the correlation results according to the following equation adopted from the literature [11].

$$\log \sigma = a + b \log \text{TLL} \quad (2)$$

where *a* and *b* are correlation parameters. The above equation provides a good fit to the experimental data.

4. Conclusion

An increase in molecular mass of PEG from 3500 to 20 000 causes the expansion of the two-phase area. The interfacial tension of the PEG 4000 (1)–K₂HPO₄ (2)–water (3), PEG 6000 (1)–K₂HPO₄ (2)–water (3) and PEG 20 000 (1)–K₂HPO₄ (2)–water (3) systems at 298.15 K increases with an increase in TLL and molecular mass of PEG. The effect of temperature on the interfacial tension is small when systems with the same tie-line length are compared.

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