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Publisher Taylor & Francis

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Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646857>

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Online publication date: 10 December 2010

To cite this Article Azimaie, R. , Pazuki, G. R. , Taghikhani, V. , Vossoughi, M. and Ghotbi, Cyrus(2010) 'Liquid-liquid phase equilibrium of MgSO_4 and PEG1500 aqueous two-phase system', Physics and Chemistry of Liquids, 48: 6, 764 – 772

To link to this Article: DOI: 10.1080/00319100903046112

URL: <http://dx.doi.org/10.1080/00319100903046112>

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Liquid–liquid phase equilibrium of MgSO₄ and PEG1500 aqueous two-phase system

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(Received 28 December 2008; final version received 16 May 2009)

In this work, PEG 1500, MgSO₄ and water were used to create an aqueous two-phase system and the effect of temperature was surveyed by obtaining binodal data and equilibrium data at 35, 40 and 45°C; compositions of mixture were obtained by atomic absorption spectrometer and refractometry method. Results showed that with increasing temperature, the solution tends to attain a two-phase region and the slope and length of tie lines increases. Modified Wilson equation was used to correlate this system, adjustable parameters were evaluated directly from experimental data and good agreement with experimental data was obtained. The overall average relative deviation was found to be less than 6%.

Keywords: aqueous two-phase systems; polymer; salt; Wilson-NRF model; LLE

1. Introduction

In 1986, Albertson first showed that the biological component within aqueous two-phase systems (ATPS) can be separated [1]. The ATPS were widely used for separation and purification of biomolecules such as protein, DNA, viruses, etc. [2–4].

Aqueous two-phase systems are formed using two aqueous polymers or aqueous polymer and salt. One polymer must be hydrophobic and another polymer, or salt, hydrophilic, so that the lower phase is rich in the hydrophilic component because of its higher density in water solvent and the upper phase is rich in the hydrophobic one.

When biomolecules are added to ATPS, they cross the interface and go to another phase, because 80–95 wt% in both phases is water, due to which the interfacial tension between phases are weak and the biomolecule is not denatured. It is important that the biomolecule does not denature during separation, and the presence of polymer results in stability of the biomolecule.

A suitable system for partitioning must have two different physical properties in each phase. The parameters that affect ATPS are: (1) type of polymer and salt and their concentration, (2) electrical potential difference between two phases,

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(3) interfacial tension and relative hydrophobicity in interface, (4) ionic strength, (5) temperature and (6) pH [1,5,6].

In polymer-salt ATPS an expensive polymer like dextran, which is used in polymer-polymer ATPS is not needed. Besides, lower viscosity and higher difference in density of phases decreases the time of separation of phases [7]. However, a high concentration of salt can denature the biomaterial, and in polymer-salt ATPS, affinity partitioning does not function [8, 9].

Zafarani-Moattar and Sadeghi experimentally determined the phase diagram of the aqueous PPG 400-sodium sulfate, PPG 400-sodium carbonate and PPG 400-sodium nitrate systems at 25°C. The effect of the type of salt on the binodal and tie lines has been studied [10]. Pereira *et al.* measured the phase diagram of Ucon 50-HB-5100-ammonium sulfate-water at 30 and 40°C. A linear regression was used to correlate the slope and standard deviation for each tie line [11]. Graber *et al.* studied the effect of temperature on liquid-liquid equilibrium (LLE) in the aqueous biphasic system formed by lithium sulfate-polyethylene glycol 4000-water at 5, 25 and 45°C. The LLE experimental data were correlated to the NRTL thermodynamic model for activity coefficient with a mean deviation of 1.07% [12].

Thermodynamic behaviour of ATPS is complicated and, at present, there is a lack of experimental data on this. In this study we determine the binodal curve and tie lines of polyethylene glycol (PEG) 1500-magnesium sulfate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$)-water and correlate the experimental data with Wilson-NRF model.

2. Experimental

2.1. Materials

PEG ($\text{HO}(\text{C}_2\text{H}_4\text{O})_n\text{H}$) with a molar weight of 1400–1600 g mol^{-1} ($M_w = 1500 \text{ g mol}^{-1}$) from Merck with Art No. 807489 and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ($M_w = 240.48 \text{ g mol}^{-1}$) from Merck with Art No. 5882 were purchased. As mineral components in water do not interfere with the reaction system, deionised water was used and for this purpose, a resin deioniser was utilised.

2.2. Method

The temperature is kept constant by preparing a Jumo etron model 702044, with Pt 100 thermal probe sensor, thermal bath having a thermostat set to a precision of 0.01°C. The thermal jacket has two layers. In the inner layer, the ATPS is formed at constant temperature and in the outer layer water at a constant temperature was circulated in order to maintain constant temperature. Two lids were available in the top and the bottom of the cell for obtaining samples of the solution. A refractometer (Erma optical, made in Japan) was used to determine the weight fraction of the polymer in solution. An empirical correlation for various concentrations of PEG and MgSO_4 with their respective refractive index is obtained. The relation between the refractive index and weight percents of PEG and salt can be written as:

$$aw_p + bw_c + c = n_d, \quad (1)$$

where is the refractive index. The adjustable parameters of Equation (1) for the upper and lower phases are listed in Table 1.

Table 1. The adjustable parameters of refractive indexes equation (Equation (1)).

	<i>a</i>	<i>b</i>	<i>c</i>	OARD
Upper phase	0.0014	0.0031	1.3325	0.0029
Lower phase	0.0327	-0.0063	1.3325	0.0054

Note:
$$\text{OARD} = \left(\sum_{i=1}^N \frac{|\text{ref index}^{\text{exp}} - \text{ref index}^{\text{calc}}|}{\text{ref index}^{\text{exp}}} \right) / N.$$

The amount of MgSO_4 in aqueous solution was determined using an atomic absorption spectrometer (Varian 220A, USA) and finally a digital balance (Mettler AC 100) with precision of 0.0001 g was used to confirm the weight.

For determining the binodal curve, at first, two stock solutions of a known concentration of PEG 1500 solution and MgSO_4 solution were made, then at constant temperature, titration with MgSO_4 solution was carried out. The point at which the solution becomes cloudy during titration is the point of binodal curve called cloud point. After determining the cloud point, the titration was carried out with PEG 1500 solution. Binodal curves were determined at 35, 40 and 45°C.

For determination of the tie-lines, feed sample with appropriate amounts of PEG 1500– MgSO_4 –water was prepared in a glass cell and mixed well using magnetic stirrer for 2 h. The thermostat was set at the desired temperature and the solution allowed to separate for 6 h. Samples were carefully taken from the top and the bottom of the solution with a syringe. The concentration of PEG 1500 and MgSO_4 were determined through refractometry and atomic absorption spectroscopy, respectively.

3. Thermodynamic framework

The activity coefficient for each species in aqueous polymer solution can be obtained as:

$$\ln \gamma_i = (\ln \gamma_i)^{\text{com}} + (\ln \gamma_i)^{\text{res}}. \quad (2)$$

In this research, the Flory–Huggins model for combinatorial term and the Wilson-NRF model that is extended based on local area fraction for residual term, are used for correlation of experimental data [13].

The activity coefficient of the combinatorial term is given as:

$$\ln \gamma_i^{\text{com}} = \ln \frac{\phi_i}{x_i} + 1 - \frac{\phi_i}{x_i}, \quad (3)$$

where

$$\phi_i = \frac{x_i r_i}{\sum_j x_j r_j}. \quad (4)$$

In the above equation x_i is the mole fraction of component i and r_i is number of segment i .

Recently, Pazuki *et al.* proposed a Wilson-NRF Gibbs energy model based on local area fraction as [14]:

$$\frac{g^{\text{ex}}}{CRT} = - \sum_i \theta_i \left[\ln \left(\sum_j \theta_j H_{ji} \right) - \sum_j \theta_j \ln H_{ji} \right]. \quad (5)$$

Thus, the activity coefficient of species i in the mixture can be written as:

$$\frac{\ln \gamma_i}{C} = - \ln \left(\sum_j \theta_j H_{ji} \right) - 1 + \sum_j \frac{\theta_j H_{ij}}{\sum_k \theta_k H_{kj}} + \sum_j \theta_j \left(\sum_k \theta_k \ln \left(\frac{H_{kj}}{H_{ij} H_{ji}} \right) \right), \quad (6)$$

where

$$H_{ij} = \exp \left(- \frac{E_{ij}}{CRT} \right) \quad (7)$$

$$\theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \quad (8)$$

$$E_{ij} = h_{ij} - h_{ii} \quad (9)$$

and C is coordination number that is set to be 10.

The values for the surface and volume parameter of component i are calculated using the following equations:

$$r_i = \frac{V_i}{V_3} \quad (10)$$

$$q_i = r_i \left[1 - \frac{1}{C} \left(1 - \frac{1}{r_i} \right) \right], \quad (11)$$

where in Equation (10) V_i is the molar volume of component i and V_3 is the molar volume of water. The molar volume of the polymer has been calculated from the specific volume and the number average molar mass of polymer. The specific volume ($\text{cm}^3 \text{g}^{-1}$) of PEG and MgSO_4 are 0.833 and 0.3759, respectively [15].

The proposed model is used in correlating the phase behaviour of ATPS containing PEG 1500 and MgSO_4 .

4. Results and discussion

In this work, binodal data at 35, 40 and 45°C were measured. The data at each temperature are shown in Tables 2–4 and tie lines and binodal curves are shown in Figures 1–3. Experimental phase equilibrium has been obtained in these three temperatures that are shown in Tables 5–7. When two phases are formed in a cell, the lower phase is hazy and the two phases are clearly distinct. As is shown in Figure 1, change in temperature at this range does not make much difference between binodal curves totally and they are close to each other; however, with lower salt concentration, the binodals are crossed and the temperature effect is reversed. A similar result was obtained by Salabat *et al.* [16]. The slope and length of tie lines

Table 2. The binodal data for PEG 1500 (1) wt%, MgSO₄ (2) Wt% at $T=35, 40$ and 45°C .

$T=35^{\circ}\text{C}$		$T=40^{\circ}\text{C}$		$T=45^{\circ}\text{C}$	
1	2	1	2	1	2
41.20	0.62	36.25	1.87	38.03	1.36
37.71	0.65	30.55	2.44	35.60	1.53
34.37	1.02	28.81	2.77	29.02	1.64
33.31	1.25	17.75	4.43	22.39	2.69
29.49	1.75	16.43	4.82	17.47	3.95
27.71	2.15	15.37	5.11	14.61	4.87
27.12	2.31	14.31	5.42	12.47	5.56
26.13	2.50	13.45	5.73	10.70	6.07
25.60	2.52	12.59	6.02	9.76	6.38
24.09	2.85	11.51	6.31	8.48	6.80
13.12	6.49	11.04	6.41	7.44	7.66
6.05	10.15	10.74	6.59	7.00	8.20
4.56	15.63	9.50	7.01	3.81	14.53
4.09	16.12	8.69	7.28	4.63	19.46
4.14	16.36	7.19	7.88	5.43	22.31
4.16	16.72	6.50	8.15	6.43	27.02

Table 3. Experimental phase equilibrium for PEG 1500 (1) wt% and MgSO₄ (2) wt% at $T=35^{\circ}\text{C}$.

Overall phase		Upper phase		Lower phase	
1	2	1	2	1	2
13.25	7.00	6.05	10.15	4.16	16.72
7.99	9.30	22.68	5.14	4.09	16.12
4.78	10.04	23.21	4.09	4.14	16.36
26.80	3.64	8.76	11.93	4.56	15.63

Table 4. Experimental phase equilibrium for PEG 1500 (1) wt% and MgSO₄ (2) wt% at $T=40^{\circ}\text{C}$.

Overall phase		Upper phase		Lower phase	
1	2	1	2	1	2
4.43	17.74	20.70	4.30	4.95	21.01
7.19	15.78	28.81	2.77	6.39	28.09
9.52	8.11	30.55	2.44	6.23	27.42
9.10	13.85	36.25	1.87	5.25	21.56

increase with ascending temperature, this is because the compositions of equilibrium phases change with temperature variation. When the temperature of a solution goes up, the concentration of PEG in the upper phase will increase and this is in agreement with Voros *et al.*'s [17] work.

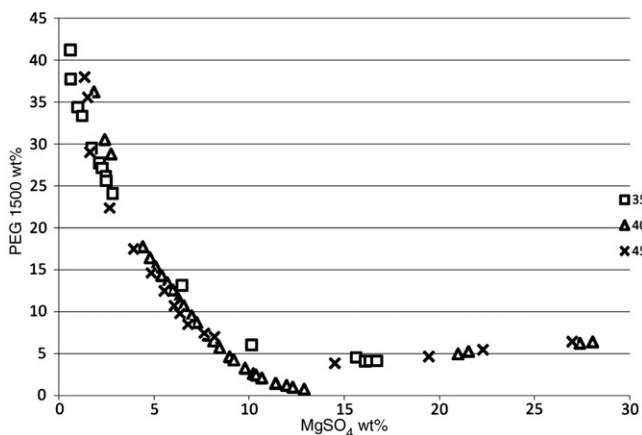


Figure 1. Binodal curve for PEG1500–MgSO₄–water at 30, 35 and 45°C.

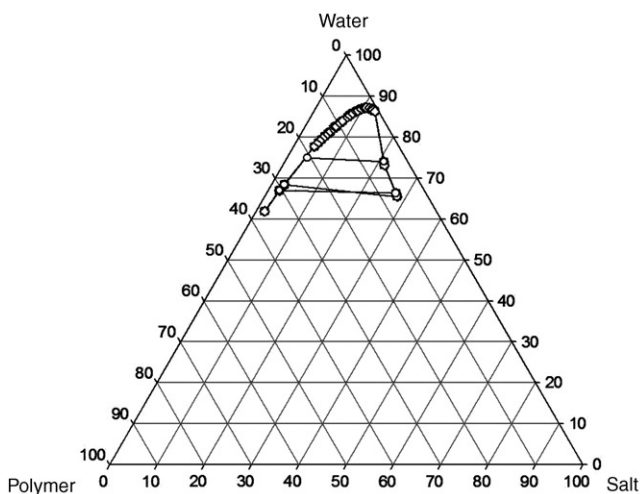


Figure 2. Triangular tie lines and binodal curve for PEG1500–MgSO₄–water at 40°C.

The Wilson-NRF model used for correlation and prediction of liquid–liquid phase behaviour of ATPS containing PEG and MgSO₄ and the experimental data correlated with NRTL model results are shown in Tables 6 and 7, respectively. Phase behaviour of liquid–liquid system is calculated using the equality of activity in two phases for all components in solution:

$$(x_i \gamma_i)^I = (x_i \gamma_i)^{II} \tag{12}$$

For optimising the interaction parameters, first the objective function obtained from equality of chemical potentials of each species in two phases is minimised:

$$F_\mu = \sum_i^N \sum_j^3 (\Delta\mu_{ij}^I - \Delta\mu_{ij}^{II})^2, \tag{13}$$

where i, j are the number of species and tie lines, respectively.

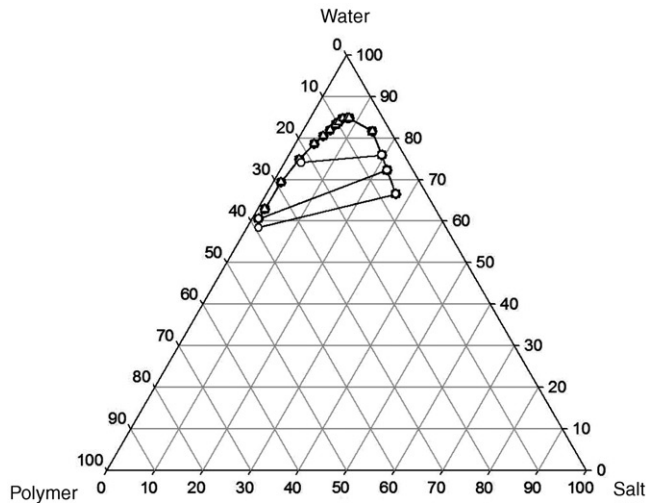


Figure 3. Triangular tie lines and binodal curve for PEG1500–MgSO₄–water at 45°C.

Table 5. Experimental phase equilibrium for PEG 1500, MgSO₄ and water at $T=45^{\circ}\text{C}$.

Overall phase		Upper phase		Lower phase	
1	2	1	2	1	2
8.98	7.78	22.38	3.51	4.63	19.46
14.63	8.31	35.60	1.53	3.81	14.53
22.70	7.71	39.11	2.46	6.43	27.02
17.72	8.28	38.03	1.36	5.43	22.31

Table 6. Adjustable parameters of PEG–MgSO₄–water ternary system and OARD% with modified Wilson model [13].

$T (^{\circ}\text{C})$	E_{12}	E_{21}	E_{13}	E_{31}	E_{23}	E_{32}	OARD%
35	416.73	-256.04	13.54	-80.25	133.52	299.43	4.49
40	310.23	-162.57	-45.06	-53.36	45.62	219.49	2.22
45	378.69	-189.62	1.61	-73.33	109.87	262.44	6.91

Table 7. Adjustable parameters of PEG–MgSO₄–water ternary system and OARD% with NRTL model.

$T (^{\circ}\text{C})$	τ_{12}	τ_{21}	τ_{13}	τ_{31}	τ_{23}	ϕ_{32}	OARD%
35	7.49	19.30	2.16	18.10	61.31	3.10	3.97
40	7.50	19.00	2.25	17.20	61.31	3.29	3.89
45	8.69	14.63	2.57	18.92	61.33	3.58	8.15

The points obtained from minimisation of Equation (15) may be related to maximum or saddle points. Therefore, the following objective function is used for optimising the interaction parameters:

$$F_w = \sum_k^M \sum_i^3 \sum_j^2 \left(w_{ijk}^{\text{exp}} - w_{ijk}^{\text{cal}} \right)^2, \quad (14)$$

where w is the weight fraction of each species and superscripts 'cal' and 'exp' refer to calculated and experimental data. The adjustable parameters of PEG–MgSO₄–water ternary system have been obtained using Nelder–Mead optimisation method [18] by minimising Equation (15).

$$OARD = \frac{1}{6N} \sum_{k=1}^N \sum_{j=1}^2 \sum_{i=1}^3 \frac{|w_{ijk}^c - w_{ijk}^e|}{w_{ijk}^e} * 100, \quad (15)$$

where 1, 2 and 3 represent PEG 1500, MgSO₄ and water. The results of correlation and OARD are shown in Tables 6 and 7 and both models illustrate good agreement between experimental data and calculation data.

5. Conclusions

Liquid–liquid equilibrium data for PEG 1500–MgSO₄–water at 35, 40 and 45°C were obtained. Experimental data shows that with increasing temperature, the two-phase envelope expands and where there is rich concentration of polymer and dilute concentration of salt, sensitivity to temperature increases, but when the polymer is dilute with a rich concentration of salt, a change in temperature causes no change in the two-phase region. At constant temperature, high concentration of salt and low concentration of polymer, the two-phase region widens. Data reported from Voros *et al.* [17] confirm this opinion. Thus, change in temperature has no evident influence at phase behaviour; however, with lower salt concentration, the binodals cross each other and the temperature effect is reversed. The effect of temperature has been seen on tie lines also; compositions of equilibrium phases change with temperature variation and therefore slope, and the length of tie lines increase with ascending temperature.

Generally, in rich PEG region, a decrease in temperature causes an increase in the two-phase region and because of this fact, with decreasing of temperature, repulsion between molecules of PEG increases. In a salt rich solution, the behaviour of the binodal curve depends on type of salt, that is, ions from salt have different behaviour when temperature changes [19].

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