

# Liquid–liquid equilibria of aqueous two phase system containing of PEGDME and $(\text{NH}_4)_2 \text{SO}_4$ at different temperatures and its application in partitioning of lactic acid

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## ABSTRACT

In this work, the liquid-liquid equilibria (LLE) of (PEGDME2000 + ammonium sulphate + water) was studied at  $T = (298.15, 308.15 \text{ and } 318.15) \text{ K}$ . Furthermore for this system the free energies, enthalpies and entropies of cloud points were calculated at the mentioned temperatures in order to investigate the driving force for the mentioned two-phase system. For representing the experimental binodal data the Merchuk equation in the original form and with the temperature dependency and an empirical equation were used. Othmer-Tobias and Bancraft, a temperature dependent Setschenow and osmotic virial equations were used to fit the tie-line data. Moreover, the effect of temperature on the binodal curves and the tie-lines for the investigated aqueous two-phase system have been studied. In addition the partitioning behaviour of the lactic acid molecule on the investigated aqueous two-phase system was studied.

**Keywords:** (Liquid–liquid) equilibrium; Polyethylene glycol di-methyl ether; Ammonium sulphate; Setschenow equation; Lactic acid

## 1. Introduction

ATPSs have been recognized as an economical and efficient downstream processing method, and widely used for recovery and purification of various biomolecules [1]. In this work liquid-liquid equilibrium (LLE) of aqueous two-phase systems containing PEGDME2000 and ammonium sulphate has been studied. Lactic acid is one of important

carboxylic acids in chemical industries. Partitioning of lactic acid in the above two phase system has also been studied.

## 2. Experimental

### 2.1. Materials and methods

Poly ethylene glycol di-methyl ether (PEGDME), of molar mass 2000, with CAS number 9003-39-8, was obtained from Merck. Ammonium sulphate with CAS Registry No. 7783-20-2 and minimum mass fraction purity 0.99 was obtained from Merck. The polymer and salt were used without further purification, and double distilled deionized water was used. Concentrated lactic acid solution (mass fraction 98% in water) with CAS number 79-33-4, was obtained from Sigma aldrich. A glass vessel with an external jacket used around which water at constant temperature was circulated using a thermostat with an uncertainty  $\pm 0.05$  K. The bimodal curves were determined by clouding point titration method. In this method, the composition of the mixture for each point on the binodal curve was determined from the amount of titrate added until turbidity was observed using an analytical balance (Shimatzu, 321-34553, Shimatzu Co., Japan) with a precision of  $\pm 1.10 \cdot 10^{-7}$  kg. The maximum uncertainty was found to be  $\pm 0.002$  in determining the mass fraction of both polymer and salt by using of this method.

### 2.2. Procedure route

For determination of the tie-lines, feed samples (about  $2 \times 10^{-5}$  m<sup>3</sup>) were prepared by mixing appropriate amounts of polymer, salt and water in the vessel. The thermostat was set at the desired temperature, and the samples were stirred for 1 h. Then, the samples were placed in the thermostat (JULABO model MB, Germany) with temperature control ability of  $\pm 0.02$  K and allowed to settle for at least 48 h so that they could be separated into two clear phases. After the separation of the two phases, the concentrations of ammonium sulphate in

the top and bottom phases were determined by the formaldehyde method. The chemical reaction is as follows:  $2(\text{NH}_4)_2\text{SO}_4 + 6\text{HCHO} \rightarrow 2\text{H}_2\text{SO}_4 + (\text{CH}_2)_6\text{N}_4 + 6\text{H}_2\text{O}$ . The sulfuric acid formed was titrated against sodium hydroxide solution. The analysis of samples with given composition of PEGDME and  $(\text{NH}_4)_2\text{SO}_4$  showed that the presence of PEGDME did not interfere with the determination. The uncertainty in the measurement of the mass fraction of the salt is 0.002. The concentration of PEGDME in both phases was determined by refractive index measurements performed at  $T = 298.15$  K using a refract meter (ATAGO DR-A1, Japan). The uncertainty in refractive index measurement is 0.0002. Since concentrated lactic acid solution contains high levels of dimers, it was first diluted 10-fold and then boiled for (8 to 10) h under reflux to hydrolyze the dimers. The resulting solution after reflux, titrated by 0.1N potassium hydroxide.

### 3. Results and discussion

The obtained binodal data were fitted to the following empirical relationship developed by Merchuk: [2]

$$w_1 = a \exp(bw_2^{0.5} - cw_2^3) \quad (1)$$

where  $w_1$  and  $w_2$  are the concentrations of polymer and salt, respectively. The results are reported in Table 1.

**Table1:** Values of parameters (a ,b, c) and standard deviation (sd) of Eq. (1), for {PEGDME2000 (1) + ammonium sulphate (2) + water (3)} systems at different temperatures.

<i>T/K</i>	<i>a</i>	<i>b</i>	<i>c.10<sup>4</sup></i>	<i>sd</i>
298.15	110.0920	-0.5682	3.6035	0.35
308.15	97.4627	-0.5314	4.5387	0.20
318.15	105.0797	-0.5228	5.6350	0.22

On the basis of obtained standard deviations, we conclude that the Eq. (1) can be satisfactorily used to correlate the binodal data of the investigated system. The correlation equations given by Othmer- Tobias (eq2a) and Ban craft (eq 2b) [3] have been used to correlate the tie-line compositions.

$$\left(\frac{1-w_1^t}{w_1^t}\right) = k \left(\frac{1-w_2^b}{w_2^b}\right)^n \quad (2a)$$

$$\left(\frac{w_3^b}{w_2^b}\right) = k_1 \left(\frac{w_3^t}{w_1^t}\right)^r \quad (2b)$$

where, k, n, k1, and r represented fit parameters, “top” and “bot” represent top and bottom phases, respectively. These equations have also been used to assess the reliability of LLE data. The corresponding correlation coefficient values, R are given in Table 2. On the basis of the obtained deviations (Dev.), we conclude that Eqs. (2a) and (2b) can be satisfactorily used to correlate the tie-line data of the investigated system. From the correlation coefficient values, reported in Table 2, we conclude that the reported tie-line data have acceptable consistency. [4].

### 3.1. Setschenow type equation:

The following Seteschenow type equation proposed by Hey et al. [5] was also used for the correlation of tie-line data:

$$\ln\left(\frac{C_p^{top}}{C_p^{bot}}\right) = k_p + k_s (C_s^{bot} - C_s^{top}) \quad (3)$$

in which the  $k_s$  is the salting-out coefficient,  $k_p$  is a constant, and  $C_p$  and  $C_s$  are the molality of polymer and salt respectively. Recently [4] we successfully used the Eq. (3) for the

correlation of tie-line data. In this work, for the temperature dependency of fitting parameters of Eq. (3), we adopted a simple form for each parameter as follows [5]:

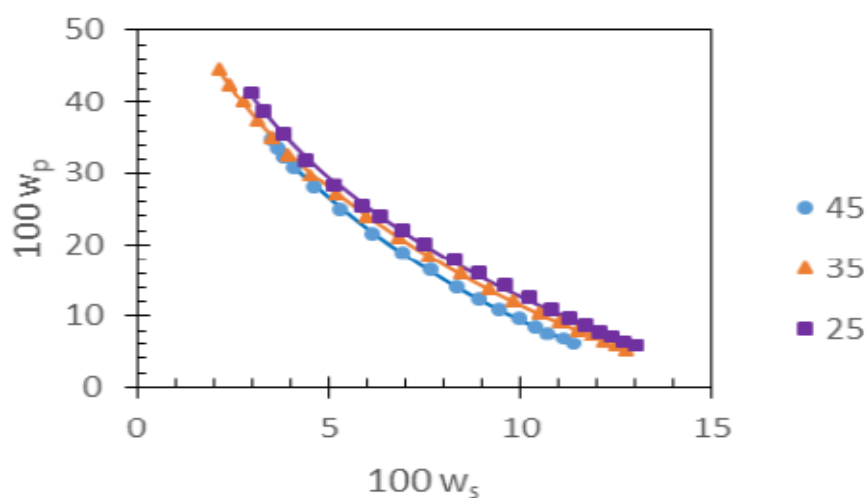
$$\ln\left(\frac{C_p^{top}}{C_p^{bot}}\right) = \left[ \frac{k_p}{T} + \frac{k_s}{T} (C_s^{bot} - C_s^{top}) \right] \quad (4)$$

The parameters of the Eq. (4) were obtained from the correlation of the experimental LLE data.

**Table 2:** Values of parameters of Othmer-Tobias and Bancroft, ( $k$ ,  $n$ ,  $K$ ,  $r$ ), for {PEGDME2000 (1) + ammonium sulphate (2) + water (3)} at different temperatures.

$T/K$	$k$	$n$	$R^2$	$K$	$r$	$R^2$	$Dev$
298.15	0.1902	1.6423	0.994	2.7652	0.6290	0.994	0.37
308.15	0.1051	1.7177	0.999	3.7313	0.5670	0.999	0.08
318.15	0.1690	1.5326	0.997	3.2655	0.6375	0.997	0.09

The locus for the experimental binodals shown in Fig. 1 demonstrated that the two-phase area is expanded with an increase in temperature.



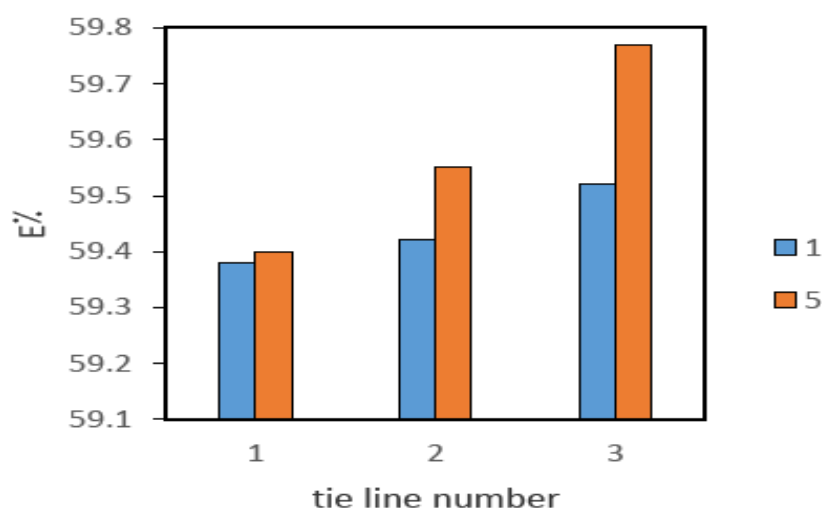
**Fig 1.** Experimental binodal results for the {PEGDME2000 (p) + di-sodium hydrogen citrate (s) + water (w)} system at different temperatures: (●)  $T = 298.15$ ; (▲)  $T = 308.15$  and (■)  $T = 318.15$  K, and (solid line) the calculated from equation (1).

### 3.2. Partition behavior of lactic acid in different temperatures:

The partition coefficients ( $K_{\text{lactic acid}}$ ) and extraction efficiency ( $E$ ) of lactic acid in aqueous two phase system were calculated respectively by Eq. (5) and Eq. (6) and presented in figure 2.

$$K_{\text{lactic acid}} = \frac{w_{\text{lactic acid}}^{\text{top}}}{w_{\text{lactic acid}}^{\text{bot}}} \quad (5)$$

$$E = \frac{K_{\text{lactic acid}}}{K_{\text{lactic acid}} + 1} \times 100 \quad (6)$$



**Fig 2.** Effect of temperature and TLL on the iodine partitioning for {PEGDME2000 (p) + (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (s) + H<sub>2</sub>O (w)} system: (1) T = 298.15 K; (2) T = 308.15 K and (3) T = 318.15 K.

This figure shows that the partition coefficient increases with increasing temperature

## 4. Conclusions

Liquid–liquid equilibrium data for the {PEGDME2000 + ammonium sulphate + water} system was studied at T = 298.15, 308.15 and 318.15 K and the experimental binodal and tie-line data at the mentioned temperatures were reported. Comparison between the experimental

data shows that the phase-separation ability of the studied system increased with increasing the temperature. The experimental binodal data were satisfactorily correlated using an empirical equation and the Merchuck equation as a function of temperature with a linear temperature dependency in the form of  $(T - T_0)$  K as a variable. Acceptable consistencies of the experimental tie-lines are obtained using the Othmer-Tobias and Bancroft equations. Additionally, Seteschenow type equation and osmotic virial model were used for the correlation of the (liquid - liquid) phase behaviour of the system studied.

On the base of the obtained results, it can be concluded that, the performances of all the considered models in the correlation are good. The Setschenow type equation with only two-parameters however, shows the best results in the correlation and prediction of the tie-line compositions of the studied system.

Applicability of this polymer based ATPS has been studied for extraction of lactic acid. We found that this ATPS which is environmentally benign can be used as a simple technique for extraction of lactic acid; so that it can efficiently extract lactic acid in polymer phase. The partition coefficients and extraction percent of lactic acid in this ATPS were obtained; and it was found that these quantities increase as the differences in PEGDME concentrations between the phases increases. From the experimentally determined values for the lactic acid molecule partitioning we concluded that partition coefficients is increased with increasing temperature.

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