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Research Article

The effect of polymer molar mass on the aqueous two-phase system containing Poly ethylene glycol dimethyl ether and ammonium sulphate and its application of this system in partitioning of iodine

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ABSTRACT

The partitioning of iodide was studied in an aqueous two phase system (ATPS) comprised of ammonium sulphate, poly ethylene glycol dimethyl ether (PEGDME), and water at 298.15 K. To investigate the effect of molar mass of the polymer on the tie-line, similar measurements were also made at T=298.15 K on this two phase system consisting of the PEGDME with molar masses of 250, 500 and 2000 g.mol^{-1}. Finally the effect of molar mass of polymer on the binodal of {PEGDME + ammonium sulphate +water} was studied by measuring liquid-liquid equilibrium at T= 298.15 K for three different molar masses. The experimental binodal data were described using two empirical nonlinear three parameter expressions developed by Merchuk and Zafarani Moattar et al. The increase in the polymer molar mass provides ATPS with larger biphasic region. The tie-line compositions were estimated and correlated using the Othmer–Tobias and Bancroft and Setschenow type equations. In addition the partitioning behavior of the iodine molecule on the investigated aqueous two-phase system was studied.

Keywords: Liquid-liquid equilibrium; Ammonium sulphate; Setschenow type equation; Poly ethylene glycol; dimethyl ether; Iodine Partitioning.

1. Introduction

Aqueous two phase systems (ATPSs) are increasingly being used in biotechnology for the separation of a wide variety of products. Separation of biological molecules and particles using ATPS was initiated more than half a century by P.-Å. Albertsson [1]. In this work, the binodal and tie-line data are reported for {PEGDME +ammonium sulphate +water} at different molar masses of PEGDME and at 298.15. We also reported iodine partitioning using {PEGDME+ (NH4)2SO4 + H2O} system and reported iodine partition coefficient in this aqueous two-phase system at T= 298.15K.

2. Experimental

2.1. Materials and method

The chemicals poly ethylene glycol di-methyl ether (PEGDME) with molar mass 2000 g.mol-1, 500 g.mol-1, and250 g.mol-1 with CAS number 9003-39-8, ammonium sulphate with CAS Registry No. 7783-20-2 purity of 99%, iodine (I2), of molar mass 253.809 g.mol-1, with CAS number 9003-39-8 and purity of 99%, were all obtained from Merck. A glass vessel with an external jacket used around which water at constant temperature was circulated using a thermostat with an uncertainty±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 ±1.10-7 kg. The maximum uncertainty was found to be ± 0.002 in determining the mass fraction of both polymer and salt by using of this method. For determination of the tie-lines, feed samples (about 2×10-5 m3) 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 ±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(NH4)2SO4+ 6HCH0 = 2H2SO4 + (CH2)6N4 + 6H20 The sulfuric acid formed was titrated against sodium hydroxide solution. The analysis of samples with given composition of PEGDME and (NH4)2SO4 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. The mixture with the same amount of polymer, salt and water used for tie-lines determination were prepared again and the partitioning 0.0014 g of iodine was investigated. The quantity of the iodine is determined by titration with sodium thiosulfate.

3. Results and discussion

For the aqueous (PEGDME + ammonium sulphate) system, the binodal data and tie-line compositions determined experimentally at different polymer molar masses and at 298.15 K temperature.

The locus for the experimental binodals is shown in Fig. 1. In fact by increasing molar mass of PEGDME, the polymer becomes less hydrophilic and its solubility in water decreases; therefore, the salting out strength of PEGDME is increased by increasing molar mass of polymer. Also, in Fig.2 the tie-line data are shown at molar masses M = (2000, and 250) g.mol-1 for the temperature 298.15 K. From Fig.2, it can be seen that the slope and length of tie-lines increased with an increase of polymer molar mass.

In this work for the correlation of binodal data, we examined the performances of the Merchuck equation [2] and the empirical equation that we proposed recently [3]:

$$w_p = a\,.exp\,[b.(w_s)^5 - c.(w_s)^3] \qquad (1)$$

$$w_p = a + \beta\ .\ \ln(w_s) + \gamma\,.w_s \qquad (2)$$

where wp and ws are the mass percent of the polymer and salt respectively. Also a, b, c are fitting parameters of Eq.(1) and α, β and are the fitting parameters of Eq. (2).

The fitting parameters for these equations along with the corresponding standard deviation for each polymer at 298.15 K are given in Tables 1 and 2. The obtained standard deviations (sd) show that both of equations (1) and (2) can be used to reproduce the binodal values; however, on the basis of the obtained standard deviations, we conclude that the performance of equation (2) is better than equation (1).

Table1: Values of parameters (a , b, c) and standard deviation (sd) of Eq. (1), for {PEGDME2000 (1) +ammonium sulphate (2) + water (3)} systems with difference in molar mass at T=298.15 K.

polymer	***a***	***b***	**$10^4.c$**	***sd***
2000	110.0920	-.5682	3.6035	0.35
500	82.6271	-.3635	9.2403	0.11

Table2: Values of parameters (α, β), and standard deviation (sd) of Eq. (2), for {PEGDME2000 (1) +ammonium sulphate (2) + water (3)} systems with difference in molar mass at T=298.15 K.

polymer	α	β	γ	*sd*
2000	64.5855	-20.2629	-.5027	0.24

For the correlation of LLE data of polymer + salt + water system, several models have been developed. However, in this work we decided to use a Seteschenow type equation [4].

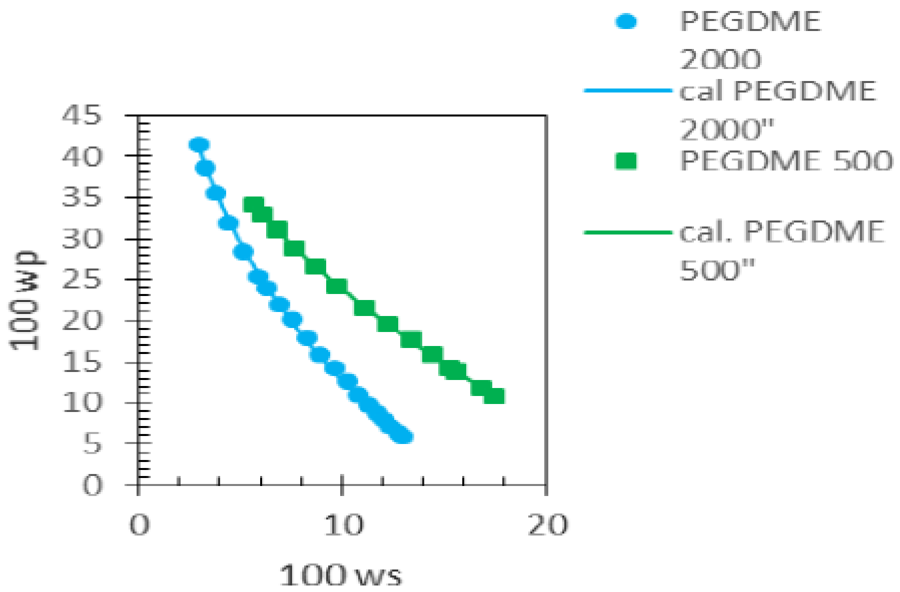

Fig 1. Plot of mass percent polymer against mass percent salt to show binodal curves for the {PEGDME (p) + ammonium sulphate (s) + water (w)} two-phase system at different polymer molar masses: (●) PEGDME2000; (■) PEGDME500; and T =298.15 K; and (solid line) the calculated from equation (1).

A Setschenow type equation is a relatively simple two parameter equation:

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

in which ks is the salting-out coefficient, kp is a constant and mp and ms are the molality of polymer and salt, respectively. Superscripts ‘‘top” and ‘‘bot” stand for polymer rich phase and salt rich phase, respectively. The fitting parameters obtained from the correlation of the experimental LLE data at T = 298.15 K are given in Table 3 along with the corresponding standard deviations. On the basis of deviations reported in Table 3, it is interesting to note that equation (3) with only two parameters represents the experimental LLE values with excellent accuracy.

Table 3: Values of parameters of Setschenow type equation, (kp, ks) (kg . K . mol-1), for {PEGME (p) + ammonium sulphate (s) + water (w)} at different molar masses and temperatures 298.15 K.

polymer	k_p	k_s	*sd*
2000	1.8025	0.8564	0.07
500	1.0469	0.3930	0.02
250	0.8197	0.4532	0.001

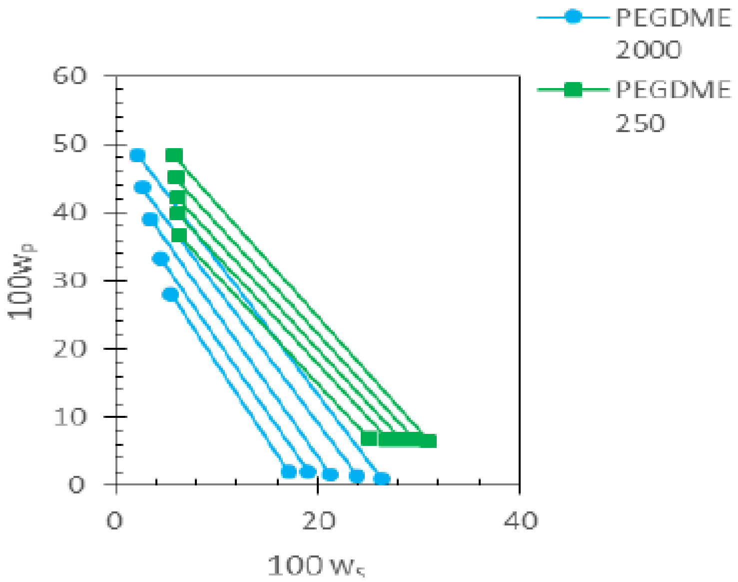

Fig.2: Effect of type of polymer via plot of mass percent polymer against mass percent salt to illustrate the effect of polymer molar mass on the slope and length of tie- lines of the {PEGDME n (p) + ammonium sulphate (s) + H_2O (w)} system: (●) PEGDME2000; (■) PEGDME250; (—), tie-lines were obtained by connecting the experimental equilibrium phase composition values.

Influence of polymer molar mass on partition behavior of I_2:

The partition coefficients (Kiodine) and extraction efficiency (E) of I_2 in aqueous two phase system were calculated respectively by Eq. (4) and Eq. (5) and the results are presented in figure 3.

$$K_{iodine} = \frac{w_{iodine}^{top}}{w_{iodine}^{bot}} \quad (4)$$

$$E = \frac{K_{iodine}}{K_{iodine}+1} \times 100 \quad (5)$$

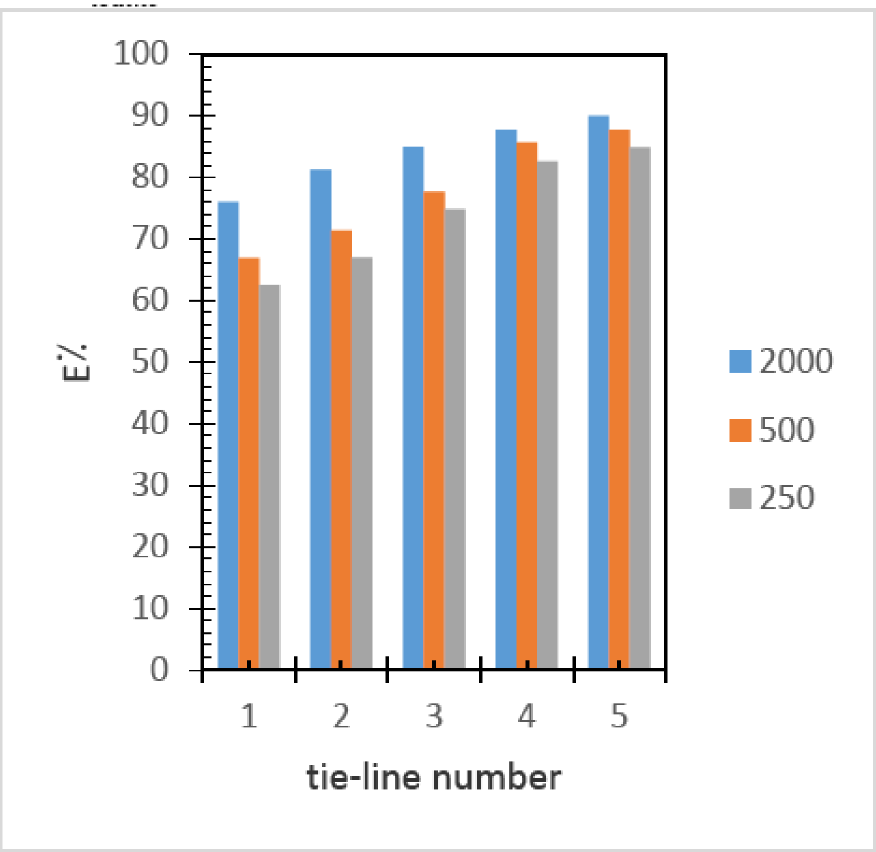

Fig.3: Effect of temperature and TLL on the iodine partitioning for {PEGDME2000 (p) + (NH4)2SO4 (s) + H2O (w)} system: (blue column) PEGDME2000; (orange column) PEGDME500 and (gray column) PEGDME250. This figure shows that the partition coefficient increases with increasing molar mass of polymer.

4. Conclusions

Phase equilibrium results were obtained for aqueous two- phase system (PEGDME+ (NH4)2SO4 +H2O) at T =298.15 K and PEGDME molar masses of 2000, 500, 250 g.mol^{-1}. The experimental binodal data were satisfactorily correlated with Merchuck and a new empirical equation. Acceptable consistencies of the experimental tie-lines are obtained using the Othmer-Tobias and Bancroft equations. Additionally, Seteschenow type equation was used for the correlation of the (liquid - liquid) phase behaviour of the system studied with excellent accuracy. Applicability of this polymer based ATPS has been studied for extraction of iodine. The partition coefficients and extraction percent of iodine in this ATPS were obtained; and it was found that by increasing molar mass of polymer the Kiodine and E are increased.

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