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Aqueous two-phase system of poly ethylene glycol dimethyl ether 2000 and sodium hydroxide at different temperatures: Experiment and correlation

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ABSTRACT

In this research, liquid–liquid equilibria (LLE) data were determined for an aqueous two-phase system containing polyethylene glycol dimethyl ether 2000 ($PEGDME_{2000}$) + sodium hydroxide + H_2O at T = 298.15, 308.15 and 318.15 K. The experimental binodal data were described using two empirical nonlinear three parameter expressions developed by Merchuk and Zafarani-Moattar. The effect of temperature on the binodal and tie-lines of the investigated aqueous two-phase system (ATPS) were also studied. Moreover, the modified local composition segment-based NRTL (the extended NRTL and the modified NRTL) and Wilson models (the extended Wilson and the modified Wilson) and also a temperature dependent Setschenow-type equation were used to fit the tie-line data points. In addition, the effect of the polymers $PEGDME_{2000}$ and poly ethylene glycol 2000 on the phase forming ability were studied. Also, the free energies of cloud points for this system were calculated from which it was concluded that the increase of the entropy is driving force for formation of studied aqueous two-phase system.

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1. Introduction

Systems containing two liquid phases at certain critical concentrations are very useful to extract and recovery many kinds of molecules of biotechnological interest, such as proteins, peptides and other small bioactive molecules [1,2]. To preserve the structure and the functional of such compounds, biphasic systems composed of two aqueous-rich phases are more appropriate than those formed by one aqueous and an organic phase. Factually, their high content in water implies a better biocompatibility and lower values of interfacial tension, thus minimizing the degradation of biomolecules during their transfer from one phase to the other. These liquid–liquid systems are formed by adding either two structurally different hydrophilic polymers or one polymer and one inorganic salt to water.

Polyethylene glycol (PEG) which is a hydrophilic polymer has been used in the aqueous two-phase partitioning studies [3]. Poly ethylene glycol dimethyl ether 2000 ($PEGDME_{2000}$) has a similar structure to the poly ethylene glycol. Thus, PEGDME can be used to form aqueous two-phase systems (ATPSs) with kosmotropic (i.e. water structure) salts. As far as we know there is a few experimental LLE data for ATPSs with this polymer [4–9].

These are report on the phase behavior of {PEG + NaOH + water} system in the literatures [10,11]. Ananthapadmanaban et al. [12] reported the only binodal curve for aqueous PEG + NaOH system. Our interest in studying aforementioned system is due to the fact that the in the similar aqueous two-phase system containing PEG and NaOH we observed phase inversion behavior [10] and therefore we would like to see whether the system {PEGDME + NaOH + water} also show similar behavior or not.

In this work, the binodal and tie-line data are reported for {$PEGDME_{2000}$ + sodium hydroxide (NaOH) + water} at T = 298.15, 308.15 and 318.15 K, that have not been published, previously. Furthermore, plait points of system have been calculated in each temperature using linear least squares regression method; and based on cloud point values the free energies of the clouding process have been estimated. In addition, the effect of the polymers $PEGDME_{2000}$ and PEG_{2000} on the phase forming ability was studied.

For reproducing the experimental binodal data two empirical nonlinear expressions [6,13] were used. The experimental tie-line composition obtained at the noted temperatures were fitted to the Othmer–Tobias and Bancraft [14], Setschenow-type equations [15], and two version of NRTL (extended NRTL [16], and modified NRTL [17]), and Wilson (extended Wilson [18], and modified Wilson [19]) models.

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Table 1
A brief summary of the purity of the used materials.

Material[a]	Molecular formula	Mass fraction purity
Poly ethylene glycol dimethyl ether2000	$CH_3O(C_2H_4O)_nCH_3$	>0.99
Poly ethylene glycol 2000	$HO(C_2H_5O)_nH$	>0.99
Sodium hydroxide	NaOH	>0.99

[a] All the these materials were supplied from Merck.

Table 2
Values of the parameters of Eq. (1), a_i, for {PEGDME$_{2000}$ (p) + sodium hydroxide (ca) + water (w)} system.

Material	Constant	Value	C *Range* (w/w)	*R*[a]
PEGDME$_{2000}$	a_p	0.1311	0–0.10	0.9999
NaOH	a_s	0.2570	0–0.08	0.9999

[a] where, *R* represented respective correlation coefficient value of the linear calibration plot of the refractive index against mass fraction for PEGDME$_{2000}$ and NaOH at the mass fraction range (*C range*) of each material.

2. Materials and methods

2.1. Materials

PEGDME$_{2000}$ with CAS Registry No. 24991-55-7 AndPEG$_{2000}$ with CAS Registry No.25322-68-3 were obtained from Merck. The number average molar mass of the polymer previously determined [4] to be 2305 g mol^{-1}, using gel permeation chromatography (GPC, Agilent, USA). Sodium hydroxide (NaOH) with CAS Registry No. 1310-73-2 and purity of min. 99% by mass were supplied from Merck. The purity of the used materials is shown in Table 1.The polymer and sodium hydroxide were used without further purification and double distilled deionized water with specific conductivity less than 0.98 μs cm^{-1} was used for preparation of solution.

2.2. Apparatus and procedure

The apparatus employed for the determination of the experimental LLE data of the studied ternary system is essentially similar to the one used at previous works [4–6]. A glass vessel with volume about 50 cm^3 was used to carry out the phase equilibrium determination. An external jacket placed in glass vessel and water at constant temperature was circulated using a thermostat around this jacket. The temperature was controlled to within ±0.05 K. The binodal curves were determined by clouding point titration method. A stock sodium hydroxide solution was prepared and diluted to have a solution of 0.1 M; since in weighing solid NaOH it can absorb some water, to determine the exact concentration of prepared solution we titrated it with the standard 0.01 N HCl solution. In this method a sodium hydroxide solution of known concentration was titrated with the PEGDME$_{2000}$ solution or vice versa, until the solution turned turbid. This point indicates the formation of two liquid phases. An analytical balance (Shimatzu, 321-34553, Shimatzu Co., Japan) with a precision of $\pm 1 \times 10^{-7}$ kg was used. In accordance to the amount of titrant added until turbidity was observed, the composition of the mixture for each point on the binodal curve was calculated by mass. 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} m^3) were prepared by mixing appropriate amounts of polymer, salt and water in the vessel. The thermostat was set at a desired temperature, and the sample was stirred for 1 h. The temperature of the thermo-stated bath was controlled using a thermostat (JULABO model MB, Germany) with an accuracy of ±0.02 K, and allowed to settle for at least 48 h to separate into two clear phases. After separation of the two phases, the concentration of NaOH in both phases were analyzed using the above titration method with the standard 0.01 N HCl solution; and for further check we also determined the NaOH concentration using flame photometry method. Very Good agreement between these two methods was found. The uncertainty in the measurement of the mass fraction of the salts is ±0.002. The concentration of PEGDME in both phases was determined by refractive index measurements performed at T = 298.15 K using a refractometer (ATAGO DR-A$_1$, Japan) with a precision of ±0.0001. For dilute aqueous solutions containing a polymer and a salt, the relation between the refractive index, n_D, and the mass fractions of polymer, w_p, and salt, w_{ca} is given by:

$$n_D = n_0 + a_p w_p + a_{ca} w_{ca} \tag{1}$$

here n_0 is the refractive index of pure water which is set to 1.3325 at T = 298.15 K. This equation has been used for phase analysis of the (polypropylene glycol + NaCl + H_2O) system by Cheluget et al. [20]. We found that the same method of calculated plots and evaluation of parameters given by Cheluget et al. can also be used for analysis of studied (PEGDME$_{2000}$ + NaOH + H_2O) system. a_p and a_{ca} are constants of polymer and salt respectively, for which linear calibration plots of refractive index of the solution are obtained. However, it should be noted that Eq. (1) is only valid for dilute solutions. Therefore, it was necessary to dilute the samples before refractive index measurements, to be in the mass fraction range (*C Range*) presented in Table 2. The uncertainty of the mass fraction of PEGDME$_{2000}$ achieved using Eq. (1) was better than 0.0002.The value of these constants and respective correlation coefficient values, *R*, is given in Table 2.

3. Results and discussion

3.1. Experimental results

The binodal data and the tie-line composition for the two-phase system {PEGDME$_{2000}$ (p) + sodium hydroxide (ca) + water (w)} determined experimentally at T = 298.15, 308.15 and 318.15 K are shown in Tables 3 and 4, respectively. The effect of temperature on the phase-forming ability in the studied system is also shown in Fig. 1. The locus for the experimental binodals is shown in Fig. 1demonstrated that the two-phase area is expanded with an increase in temperature.

Table 3
Experimental binodal data in mass fraction, w_i, for {PEGDME$_{2000}$ or PEG$_{2000}$ (p) + sodium hydroxide (ca) + water (w)} systems at T = 298.15, 308.15 and 318.15 K.[a]

PEGDME$_{2000}$						PEG$_{2000}$	
T (K) = 298.15		T (K) = 308.15		T (K) = 318.15		T (K) = 298.15	
100 w_p[b]	100 w_{ca}	100 w_p	100 w_{ca}	100 w_p	100 w_{ca}	100 w_p	100 w_{ca}
46.94	1.64	45.59	1.56	47.36	1.32	25.18	4.49
44.38	1.82	42.64	1.86	43.90	1.52	24.67	4.65
40.31	2.18	38.43	2.19	38.44	1.92	23.96	4.77
35.31	2.59	34.56	2.45	34.69	2.23	22.98	4.91
31.83	2.95	30.78	2.86	30.04	2.63	22.17	5.06
27.24	3.47	27.74	3.18	26.80	2.96	20.88	5.29
23.14	3.98	23.91	3.64	24.35	3.21	19.69	5.49
19.70	4.56	17.71	4.49	20.55	3.54	18.05	5.77
17.06	4.96	15.32	4.83	18.25	3.97	16.64	6.02
14.24	5.40	12.80	5.21	15.43	4.31	14.89	6.35
11.46	5.85	10.54	5.61	13.22	4.63	12.95	6.70
				10.69	5.03	11.00	7.08

[a] Uncertainties for mass fraction and temperature are 0.002 and 0.05 K, respectively.

[b] w_p and w_{ca} represent the mass fraction of polymer and salt, respectively.

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