Effects of solid poly (ethylene glycols) addition to the solutions of aniline or *N,N*-dimethylaniline with water: Experimental measurements and modelling

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Abstract: In this work, the liquid–liquid and solid–liquid phase behaviour of ten aqueous pseudo-binary and three binary systems containing polyethylene glycol (PEG) 2050, polyethylene glycol 35000, aniline, *N,N*-dimethylaniline and water, in the temperature range 298.15–350.15 K and at ambient pressure of 0.1 MPa, was studied. The obtained temperature-composition phase diagrams showed that the only functional co-solvent was PEG2050 for aniline in water, while PEG35000 even showed a clear anti-solvent effect in the *N,N*-dimethylaniline aqueous system. The experimental solid–liquid equilibria (SLE) data have been correlated by the non-random two-liquid (NRTL) model, and the correlation results are in accordance with the experimental results.

Keywords: solid–liquid equilibria; liquid–liquid equilibria; NRTL model; polyethylene glycol; aniline; *N,N*-dimethylaniline.

INTRODUCTION

Polyethylene glycols (PEGs) are non-toxic, biodegradable polymers[1] which form strong inter- and intra-molecular hydrogen bonds,[2,3] since they are both good proton donors and acceptors.[4] PEGs, particularly in their liquid form, have wide spectrum of applications as solvents and co-solvents in organic synthesis,[5] catalysis,[2] food industry[6] and biotechnology.[7] In the previous study,[8] liquid PEGs as co-solvents for aniline and *N,N*-dimethylaniline in water were investigated, assessing possible impacts on the application of these aromatic compounds in dye industry. As a continuation, this study is investigating the possibility to use

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solid PEGs – average molecular mass 2050 (PEG2050) and 35000 (PEG35000) – in the same respect. Thus, the related temperature–composition phase diagrams of the pseudo-binary systems aniline/or *N,N*-dimethylaniline+(PEG2050 + water) and aniline/or *N,N*-dimethylaniline+(PEG35000+ water) were constructed. Diagrams showed that only the addition of PEG2050 to aqueous solution of aniline provoked a considerable co-solvent effect for aniline in water, while PEG35000 even appeared to be an anti-solvent, decreasing the solubility of water in *N,N*--dimethylaniline. The results were discussed in terms of the hydrogen bonds existing between PEGs and aniline or *N,N*-dimethylaniline but, as well, taking into account distinct solubility of PEG2050 and PEG35000 in both studied organic solvents. Binary solid–liquid equilibria (SLE) data were correlated using the non-random-two-liquid (NRTL) activity coefficient models.

EXPERIMENTAL

Materials

Studied pure compounds, their suppliers and the related stated purities are listed in Table I – all the compounds were used without further purification. Water used for preparation of the solutions was redistilled and deionized (Milipore Co. equipment, Bedford, MA). All the solutions were prepared gravimetrically using a Mettler AG 204 analytical semi-microbalance having a precision of $\pm1\times10^{-4}$ g.

TABLE I. Table of the samples (pure components) used in this study

Chemical name	Source	CAS number	Melting point range, K	Mass fraction purity	Purification method
Aniline	Sigma–Aldrich (Switzerland)	62-53-3	–	≥ 0.995	None
N,N-dimethyl-aniline	Merck (Germany)	121-69-7	–	≥ 0.99	None
Polyethylene glycol 2050	Sigma–Aldrich (Germany)	25322-68-3	325.15–327.15	≥ 0.995	None
Polyethylene glycol 35000	Sigma–Aldrich (Germany)	25322-68-3	337.15–339.15	≥ 0.995	None

Apparatus and procedure

Solid–liquid equilibria (SLE) experiments were performed in stirring-equipped, septum--closed conical Pyrex vials, in the temperature range 298.15–339.15 K and at 0.1 MPa. A visual dynamic method was applied – after slow, continuous heating, accompanied by constant stirring, the temperature at which the last solid traces disappeared was taken as that of the solid–liquid equilibrium, following the procedure applied earlier.[9-11]

Liquid–liquid equilibria (LLE) experiments were performed in the same temperature range as the SLE, using a visual method of cloud point determination, explained thoroughly in previous research.[9,12,13] The experiments were carried out in a self-made stirrer-equipped Pyrex glass cell introduced by Domanska,[14] which design and use was described in our earlier contribution.[13]

In all the experiments, a glass beaker of 2 L was used as a thermostat bath, filled with ethanol (273.15–293.15 K), water (293.15–333.15 K), or silicon oil (333.15–373.15 K) as a thermostatic liquid. Temperature was controlled using a Pt100 temperature probe, which had an accuracy of ±0.03 K.

The uncertainties in temperature determination, estimated from the repeated measurements, were never higher than ±0.5 K, except in the SLE experiments where the errors were above the aforesaid, but never exceeded ±1.0 K.

Solutions were prepared gravimetrically using a Mettler Toledo AG204 analytical semi-microbalance with the precision of $\pm 1 \times 10^{-4}$ g.

RESULTS AND DISCUSSION

PEG 2050 and PEG 35000 are solid and the first part of our study was to determine the solid–liquid phase behavior of the binary solutions (PEG 2050 + *N,N*-dimethylaniline) and (PEG35000 + aniline or *N,N*-dimethylaniline), since the system PEG2050 + aniline was studied in the previous work.[9] Thus, the experimental solid–liquid equilibrium (SLE) data of the three binary systems are listed in Table S-I of the Supplementary material to this paper.

However, the temperature-composition phase diagrams at 0.1 MPa are presented only for the system PEG2050 + *N,N*-dimethylaniline (Fig. 1) since the solubility of PEG35000 in the studied aromatic molecules is very low and unsuitable for graphical presentation.
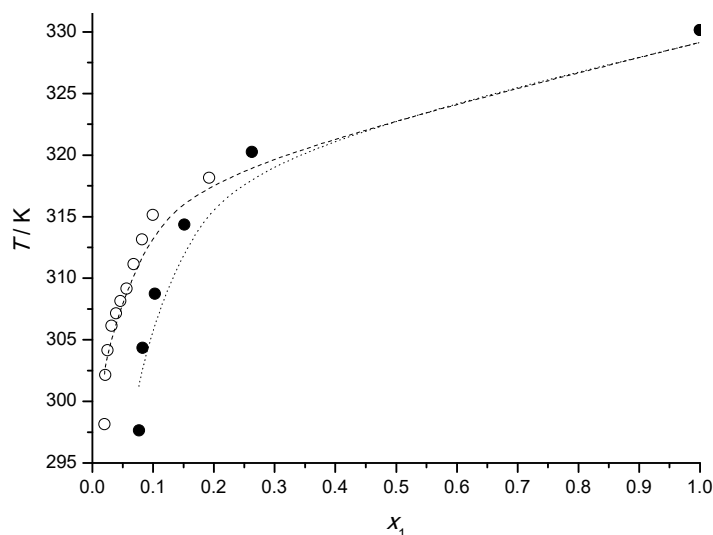

Fig. 1. Solid–liquid equilibria for the binary system (PEG 2050 + *N,N*-dimethylaniline): hollow circles – experimental data; line $(---)$ presents the correlations of these data using the NRTL model (Eqs. (1)–(4) later on). Filled circles refer to the experimental data for the binary system (PEG 2050 + aniline),[9] given for comparison; line $(\cdots)$ depicts the correlations of these data using the same NRTL model; x_1 represents mole fractions of PEG2050 in solution.

N,N-dimethylaniline is a dialkylamine, a derivative of aniline with two methyl groups bonded to the nitrogen in the amine group – thus, the hydrogen bond acidity is reduced to zero, while the same parameter for aniline is as high as 0.26.[15] Thus, being a better proton donor, aniline builds stronger hydrogen bonds with the oxygen atoms in the PEG2050 chain which are proton acceptors. This could be the reason for a better solubility of PEG 2050 in aniline than in *N,N*-dimethylaniline as it can be seen from the comparison given in Fig. 1. The impact of the polymer chain length in the studied solid–liquid phase behaviour is that the longer chain led to lower solubility in the studied organic solvents (see Table S-I). This was expected since the longer chain in polymer PEG 35000 obstructs intermolecular hydrogen bonding and dipole-dipole interactions with aniline or *N,N*-dimethylaniline.

Liquid–liquid phase demixing temperatures (cloud points) were determined for the systems aniline/or *N,N*-dimethylaniline + (water + PEG 2050) and for aniline or *N,N*-dimethylaniline + (water + PEG 35000), for different compositions of (water + PEG) mixed solvent. The experimental cloud points are listed in Tables S-II–S-V of the Supplementary material and the related temperature––composition phase diagrams of the pseudo-binary systems are shown in Figs. 2––5. These diagrams show that the only useful co-solvent effect is that for aniline in water, provoked by the addition of PEG 2050 to the aqueous aniline solution – Fig. 2. On the other hand, PEG 35000 even provoked a clear anti-solvent effect
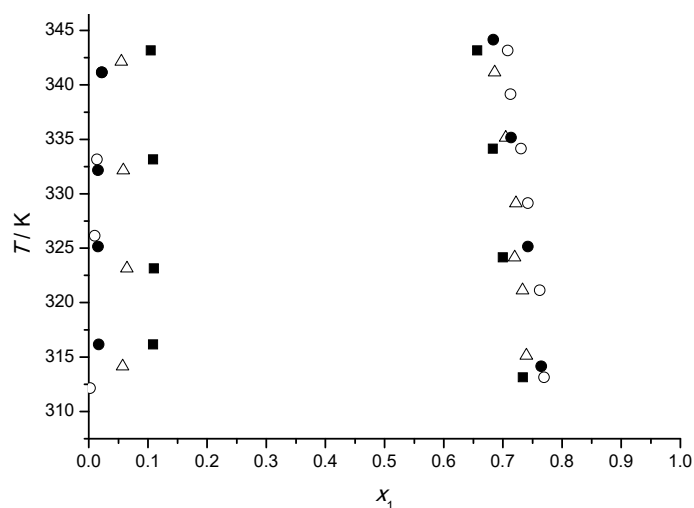

Fig. 2. Temperature–composition liquid–liquid phase diagrams at 0.1 MPa of: *i*) binary system aniline (1) + water (2),[8] hollow circles; *ii*) pseudobinary system aniline (1) + (water + PEG2050) (2), for the different mole fractions (x_{PEG}) of PEG in the combined (PEG2050 + water) solvent, filled circles, x_{PEG} = 0.0022, hollow triangles, x_{PEG} = = 0.0058, filled squares, x_{PEG} = 0.0087. x_1 represents mole fractions of aniline in solutions.

in the aqueous *N,N*-dimethylaniline, decreasing the solubility of water – Fig. 5. The aforementioned low solubility of solid PEG 35000 in the studied aromatic molecules (see Table S-I) is probably the main reason for this behaviour.
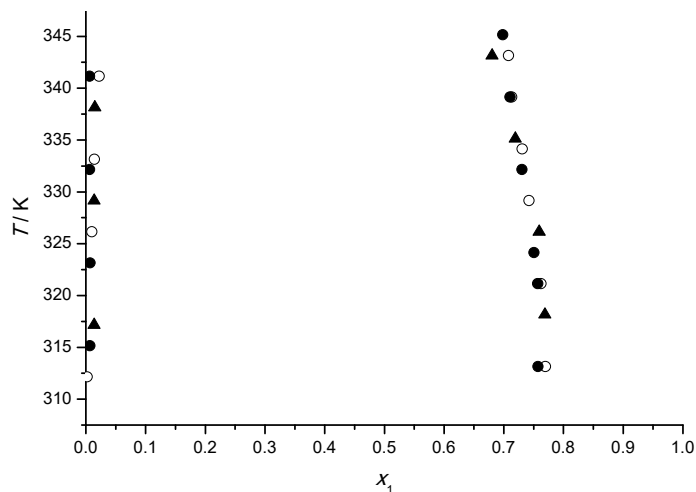

Fig. 3. Temperature–composition liquid–liquid phase diagrams at 0.1 MPa of: *i*) binary system aniline (1) + water (2),[8] hollow circles; *ii*) pseudobinary system aniline (1) + (water + PEG35000) (2) for the different mole fractions (x_{PEG}) of PEG in the combined (PEG35000 + water) solvent: filled circles, $x_{PEG} = 2.720 \times 10^{-4}$; filled triangles, $x_{PEG} = 1.285 \times 10^{-4}$. x_1 represents mole fractions of aniline in solutions.
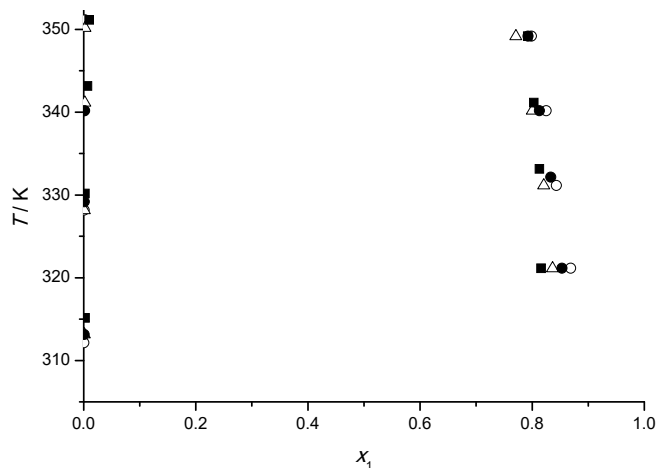

Fig. 4. Temperature–composition liquid–liquid phase diagram at 0.1 MPa of: *i*) binary system *N, N*-dimethylaniline (1) + water (2),[8] hollow circles; *ii*) pseudobinary system *N,N*-dimethylaniline (1) + (water + PEG2050) (2), for the different mole fractions (x_{PEG}) of PEG in the combined (PEG2050 + water) solvent: hollow triangles, $x_{PEG} = 0.0058$; filled circles, $x_{PEG} = 0.0022$; filled squares, $x_{PEG} = 0.0087$. x_1 represents mole fractions of *N,N*-dimethylaniline in solutions.
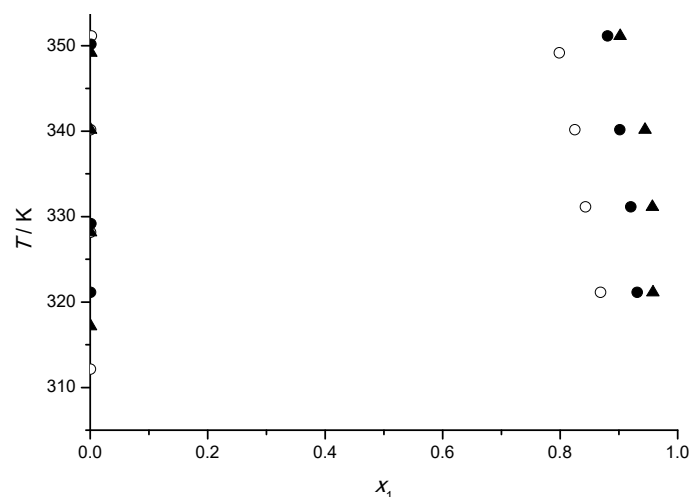
Fig. 5. Temperature–composition liquid–liquid phase diagrams at 0.1 MPa of: *i*) binary system *N,N*-dimethylaniline (1) + water (2),[8] hollow circles; *ii*) pseudobinary system *N,N*-dimethylaniline (1) + (water + PEG35000) (2), for the different mole fractions (x_{PEG}) of PEG in the combined (PEG2050 + water) solvent: filled triangles, $x_{PEG} = 2.720 \times 10^{-5}$; filled circles, $x_{PEG} = 1.285 \times 10^{-4}$. x_1 represents mole fractions of *N,N*-dimethylaniline in solutions.

MODELING OF THE BINARY SOLID–LIQUID EQUILIBRIA (SLE) DATA

The binary SLE data for the studied systems were modelled using the non-random two-liquid (NRTL) excess free energy model[16] described with the following equations:

$$\ln \gamma_1 = x_2^2 \left[\frac{\tau_{12} G_{12}}{\left(x_2 + G_{12} x_1 \right)^2} + \tau_{21} \left(\frac{G_{21}}{x_1 + G_{21} x_2} \right)^2 \right] \tag{1}$$

$$\ln \gamma_2 = x_1^2 \left[\frac{\tau_{21} G_{21}}{\left(x_1 + G_{21} x_2 \right)^2} + \tau_{12} \left(\frac{G_{12}}{x_2 + G_{12} x_1} \right)^2 \right] \tag{2}$$

$$G_{12} = \exp\left(-\alpha_{12} \tau_{12} \right), \; G_{12} = \exp\left(-\alpha_{21} \tau_{21} \right) \tag{3}$$

$$\tau_{12} = \frac{\Delta g_{12}}{RT}, \; \tau_{21} = \frac{g_{21}}{RT} \tag{4}$$

Parameter α in Eq. (3) is the NRTL excess free energy non-randomness parameter, taken herein as a constant ($\alpha_{12} = \alpha_{21} = 0.3$), which is a reasonable assumption suggested in literature[16] but as well gave the lowest deviations in the correlations. Parameters Δg_{12} and Δg_{21} are the binary interaction parameters of the NRTL model, obtained by the optimization of the objective function:

$$OF = \sum_{j=1}^{n} \left(T_j^{\text{exp}} - T_j^{\text{calc}} \right)^2 \tag{5}$$

where n is the number of experimental points, T_j^{exp} and T_j^{calc} are experimental and calculated equilibrium temperatures corresponding to the experimental mole fraction x_j. T_j^{calc} are expressed using the equation:[17]

$$\ln x_i = \frac{\Delta_{\text{fus}} H_{\text{m},i}}{RT} \left(\frac{T}{T_{\text{m},i}} - 1 \right) - \ln \gamma_i \tag{6}$$

In Eq. (6), γ_i is the activity coefficient of component i in the mixture at the corresponding temperature T, x_i is the mole faction and R is the gas constant. $T_{\text{m},i}$ is the melting temperature of the solid solute (PEG) and $\Delta_{\text{fus}} H_{\text{m},i}$ is its molar enthalpy of fusion at the same temperature. The respective values for PEG 2050 and PEG 35000 are taken from literature – PEG 2050:[9] $\Delta_{\text{fus}} H_{\text{m},i} = 370.37$ kJ mol^{-1}, $T_{\text{m}} = 330.14$ K; PEG 35000:[18] $\Delta_{\text{fus}} H_{\text{m},i} = 6650$ kJ mol^{-1}, $T_{\text{m}} = 343.15$ K.

Equation (6) considers reasonable assumptions, already applied in literature[10,11] that: *i*) the difference in the normal melting temperature and the triple point temperature is small – thus, the divergence of the enthalpies of fusion at these two temperatures can be neglected and *ii*) the impact of the difference of the heat capacities of solid and liquid solute can be neglected.

A deviation of the calculated temperature values from the experimental values is expressed as absolute average deviations ΔT, and absolute average percent deviations PD(T), for each binary system:

$$\Delta T = \frac{1}{n} \sum_{j=1}^{n} \left| T_j^{\text{exp}} - T_j^{\text{calc}} \right| \tag{7}$$

$$\text{PD}(T), \% = \frac{100}{n} \sum_{j=1}^{n} \frac{\left| T_j^{\text{exp}} - T_j^{\text{calc}} \right|}{T_j^{\text{exp}}} \tag{8}$$

The results for the binary interaction parameters and the corresponding values of ΔT and PD(T) are presented in Table II. For all four systems satisfactory results were obtained.

Graphical representation of the NRTL model is given in Fig. 1 for the systems PEG 2050 + aniline and PEG 2050 + *N,N*-dimethylaniline. The modelling of the systems involving PEG 35000 could not be graphically presented due to small solubility of PEG 35000 in the studied aromatic compounds. Total absolute average percent deviation PD(T) for all the systems was less than 0.97 %.

TABLE II. Values of the NRTL model parameters Δg_{12} and Δg_{21}, absolute average deviations ΔT and absolute average percent deviations PD(T) between experimental and calculated data for four binary systems

$-\Delta g_{12}$ / kJ kmol^{-1}	Δg_{21} / kJ kmol^{-1}	ΔT / K	PD(T) / %
PEG 2050 + aniline			
12596	9317.2	1.70	0.55
PEG 2050 + *N,N*-dimethylaniline			
9671.6	8725.2	1.10	0.36
PEG 35000 + aniline			
20339	19896	5.29	1.58
PEG 35000 + *N,N*-dimethylaniline			
26009	22103	4.88	1.49

CONCLUSION

In this study, solid–liquid equilibria data for the binary solutions of solid polyethylene glycols (average molecular mass 2050 and 35000) in aniline and *N,N*-dimethylaniline, organic aromatic solvents of common interest, were experimentally determined. Also, experimental liquid-liquid phase demixing temperatures (cloud points) in the pseudobinary systems (aniline or *N,N*-dimethylaniline + (PEG 2050 or PEG 35000 + water)) were obtained.

PEG 2050 exhibited slightly higher solubility in aniline compared to that in *N,N*-dimethylaniline, most probably due to higher hydrogen bond acidity of aniline which provided stronger hydrogen bonding with the polymer chain. On the other hand, longer polymer chain provoked dramatically lower solubility in both studied organic solvents.

The obtained liquid–liquid phase diagrams showed that only the addition of PEG 2050 to the aqueous solution of aniline provoked a considerable co-solvent effect for aniline in water. Moreover, PEG 35000 even appeared to be an anti--solvent, decreasing the solubility of water in *N,N*-dimethylaniline.

Solid–liquid equilibria data for four binary systems were correlated by NRTL model with two different temperature dependant parameters, Δg_{12} and Δg_{21}, and correlation results agree well with the experimental results.

SUPPLEMENTARY MATERIAL

Additional experimental data are available electronically from http://www.shd.org.rs/ /JSCS/, or from the corresponding author on request.

ИЗВОД

ЕФЕКТИ ДОДАВАЊА ЧВРСТИХ ПОЛИ ЕТИЛЕНГЛИКОЛА У ВОДЕНЕ РАСТВОРЕ АНИЛИНА ИЛИ Н,Н-ДИМЕТИЛАНИЛИНА: ЕКСПЕРИМЕНТАЛНА МЕРЕЊА И МОДЕЛОВАЊЕ

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Испитивана је фазна равнотежа течност–течност и чврсто–течност за десет псеудо-бинарних и три бинарна система који садрже поли етиленгликол (PEG) 2050, PEG 35000, анилин, *N,N*-диметиланилин и воду, у температурном опсегу 298,15–350,15 K и при атмосферском притиску. Добијени фазни дијаграми температура–састав показали су да је PEG 2050 једини функционални ко-растварач за анилин у води, док је PEG 35000 показао јасне анти-растварачке ефекте у воденом раствору *N,N*-диметиланилина. Експериментални подаци равнотеже чврсто–течност корелисани су помоћу NRTL модела, а добијени резултати су у складу са експерименталним резултатима.

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