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Fluid Phase Equilibria

Heat capacity and phase behaviour of aqueous solutions of triethylene glycol monopentyl ether. Two point scaling analysis

Michał Wasiak[*], Mariola Tkaczyk, Henryk Piekarski

Department of Physical Chemistry, University of Łódź, ul.Pomorska 165, 90-236 Łódź, Poland

A B S T R A C T

The specific heat capacities of triethylene glycol monopentyl ether aqueous solutions have been measured from 278.15 to 338.15 K, over the wide concentration range by DSC. The apparent and partial molar heat capacities were calculated and the two-point scaling theory was used to analyze these data. Obtained results were discussed in terms of aggregation taking place in the solution and influence of the temperature on this process. The separation line between single-phase solution and two-phase system was determined using scanning calorimetry.

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1. Introduction

Triethylene glycol monopentyl ether (C_5E_3) is a compound from the group of monoalkyl ethers of polyoxyethylene glycols with a general formula $H(CH_2)_n(OCH_2CH_2)_mOH$ (where n is number of carbon atoms in hydrocarbon chain and m is number of oxyethylene groups in hydrophilic head; abbreviated to C_nE_m).

Compounds from this group are known from their limited miscibility with water, what manifests in the phase separation above a certain temperature called *lower critical solution temperature* (*LCST*) [1—5]. Moreover, at the low concentrations of these substances, in single phase region of the solutions, the microheterogeneity of the system is frequently observed [6—9]. It is a manifestation of the formation of small aggregates and/or the micellization processes.

The calorimetric investigation of aggregation process taking place in aqueous solution of a few short-chain ionic and non-ionic amphiphiles [10—17], as well as the determination of the phase diagrams [15—17] has been reported by us previously. We showed that calorimetric method is useful in the research of such a system, and analysis of the calorimetric data can give much information about the aggregation process. The application of the two-point

scaling theory to the description of calorimetric data can also give some information on the structure of the solution [10—14].

In the literature there is a lack of information on the research on C_5E_3 mixtures with water. Especially the discussion about structural changes in C_5E_3 aqueous solutions caused by the composition of the mixture and temperature in not present. Only few papers concerning properties of pure triethylene glycol monopentyl ether — density, refractive index, boiling point [18], conformation in solid state [19] or its distribution in aqueous — dodecane solutions [20] were published.

The aim of this work was to investigate the boundaries of phase separation and aggregation process in the aqueous C_5E_3 solutions using differential scanning calorimetry.

2. Experimental

2.1. Materials

The chemical used in this work, its source and purity are presented in Table 1. Triethylene glycol monopentyl ether C_5E_3 was used as received without further distillation. C_5E_3 was stored and protected against atmospheric water and carbon dioxide. Degradation was minimized by storing amphiphile in the frozen state under inert gas. Prior to measurement, pure substance was dried over molecular sieves type 4 Å (from Lancaster) dried in vacuum at $T = 570$ K for 48 h. Deionised water was triply distilled in an argon

* Corresponding author.
  E-mail address: michalwasiak@poczta.wp.pl (M. Wasiak).

Table 1
Chemical, supplier and purity.

Chemical name	CAS No.	Supplier	Mass fraction purity	Water mass fraction
2-{2-[2-(pentyloxy) ethoxy]ethoxy}ethanol or triethylene glycol monopentyl ether abbreviation: C_5E_3	25961-91-5	Bachem	0.98	0.0003[a]

[a] Manufacturer's analysis.

atmosphere and degassed under vacuum prior to the preparation of the solutions. All solutions were prepared by weight resulting mean uncertainty in molality $2 \cdot 10^{-5}$ mol kg^{-1}.

2.2. Experimental methods

The isobaric specific heat capacities c_p were measured by means of a high sensitivity differential calorimeter Micro DSC III (Setaram, France) based on the Calvet's principle. The c_p measurements were carried out within the temperature range (278.15—338.15) K using the "continuous with reference" mode with the scanning rate 0.35 K min^{-1}. For the measurements the batch-type cell of about 1 cm^3 volume was used. As a reference substance of known heat capacity water was used [21]. Using procedure, which was described by Góralski et al. [22] the uncertainty in the c_p values can be estimated to be smaller than 0.2% with the error of the absolute temperature determination 0.05 K. To determine the critical miscibility temperature, differential heat flow (*HF*) versus temperature was recorded at a scanning rate of 0.35 K·min^{-1} using the same Micro DSC III calorimeter. In our previous research on the aqueous solutions of a few compounds from C_nE_m group, no influence the scanning rate (within 0.1—1.0 K·min^{-1}) on the phase separation temperature was found.

3. Results

3.1. Miscibility gap

The C_5E_3 exhibit limited miscibility with water with the lower critical solution temperature (*LCST*), above which the solution occurs in the form of two immiscible phases: water - rich and organic liquid - rich one. In order to determine phase diagram of the system under investigation differential scanning calorimetry was used.

The heat flow signal at the temperature, at which the phase separation occurs, exhibit rapid decreases, related with the monophasic system stability disruption due to appearance of the second phase. This phenomenon is accompanied by the increase in the heat capacity of the two-phase system compared to the single-phase system at the same temperature.

The temperature of the phase separation for each solution, within 0.35—0.96 mol kg^{-1} concentration range, was determined as an *onset-point* of the transition. The course of typical curve of *HF = f(T)* is shown in Fig. 1.

The obtained results of phase separation temperatures are presented in Table 2. The miscibility curve, for the analyzed concentration range, obtained from the calorimetric experiment is shown in Fig. 2.

Due to the temperature restrictions of the calorimetric measurements only part of the phase diagram could be presented and determination of *lower critical solution temperature* was not possible.

The *LCST* value determined by Garcia-Lisbona et al. [23] on the

basis of molecular modeling is equal to 344 K. Kahlweit et al. [24] proposed a model which allows to estimate *LCST* value on the basis of the carbon atoms number (i) in the hydrocarbon chain and a number of oxyethylene groups (j) in the amphiphile molecule, by means of the equation:

$$t_{Kahlweit}^{LCST} = (-1055 + 4282/i) + \frac{1448 - 5152/i}{1 + 1.2j}j \qquad (1)$$

Using the above equation (Eq (1).) for the C_5E_3—water system gives *LCST* value of 346.89 K. As it could be seen in Fig. 2 the experimental values of the phase separation temperatures are lower than the estimated values of *LCST*. However it is worth mentioning that comparison of experimental and calculated values of *LCST* for other C_iE_j compounds given by Kahlweit et al. [24] shows significant discrepancies. Also the *LCST* values estimated by Garcia-Lisbona et al. [23] for other similar systems differs from the experimental data up to 30 K [23].

3.2. Specific heat capacity

The measurements of specific heat capacities of C_5E_3 aqueous solutions were carried out within a concentration range from (0.0166—0.9573) mol kg^{-1}.

In Fig. 3 typical shapes of $c_p(T)$ for homogeneous solutions (middle graph) and systems in which microheterogeneity and phase separation (top graph) occurs are shown.

The specific isobaric heat capacities of solutions determined experimentally were fitted with polynomial:

$$c_p(T) = \sum_i A_i T^i \qquad (2)$$

where $c_p(T)$ is specific heat capacity at temperature T, and A_i are constants. The degree of polynomial (i) was chosen depending on the shape of the obtained experimental curve, for every solution. The values of c_p at selected temperatures were then calculated from the obtained parameters of Eq. (2). In the case of solutions with concentration exceeding 0.22 mol kg^{-1} the shape of the $c_p(T)$ had complex characteristics related with the microheterogeneity and miscibility gap. It was not possible to fit the data in the whole temperature range by one polynomial. Therefore the data was fitted locally, for each temperature range. For the solutions with concentrations above 0.68 mol kg^{-1} only the perturbations related with phase separation were observed. In those cases, data was fitted at temperatures lower than phenomenon occurs.

Specific heat capacities of C_5E_3 aqueous solution at nine chosen temperatures are shown in Fig. 4 and listed in Tables S1 in the supplementary material.

For the pure C_5E_3 obtained constants of the polynomial given by Eq. (2) in the temperature range (278.15—318.15) K are $A_0 = 2.318$ J g^{-1} K^{-1}, $A_1 = -0.00291$ J g^{-1} K^{-2}, $A_2 = 8.187 \cdot 10^{-6}$ J g^{-1} K^{-3}. These parameters give value of molar heat capacity of pure C_5E_3 at 298.15 equal to 479.8 J mol^{-1} K^{-1}, which is close to the value estimated by Góralski et al. [25] equal to 481.4 J mol^{-1} K^{-1}.

Temperature dependencies of specific heat capacity of the C_5E_3 aqueous solutions, in the concentration range between 0.22 mol kg^{-1} and 0.68 mol kg^{-1}, exhibit characteristic maxima. Similar behaviour was previously observed for the aqueous solutions of 2-butoxyethanol [26—29] and C_5E_2 [15]. Appearance of these maxima was connected with the significant changes in the process of aggregation taking place in the solution. Therefore, it seems that this conclusion may also concern the system in this work.