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Heat capacity and phase behaviour of {pentaethylene glycol monoheptyl ether + water} system. Two-point scaling approach

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ABSTRACT

The miscibility in the {pentaethylene glycol monoheptyl ether (C_7E_5) + water} system was investigated by differential scanning calorimetry (DSC). The specific heat capacities c_p of chosen nonionic amphiphile (C_7E_5) aqueous solutions have been measured within temperature range 273.15–338.15 K over wide concentration range. The apparent and partial molar heat capacities were calculated to analyze the aggregation process taking place in the solution. In order to study some additional information on the solution structure two-point scaling theory was used. On the base of temperature dependences of differential heat flow, phase coexistence curve was determined.

1. Introduction

Monoalkyl derivatives of polyethylene glycol belong to the group of nonionic surface active agents with a general formula $H(CH_2)_n(OCH_2CH_2)_mOH$ (abbreviated as C_nE_m), where n is a number of carbon atoms in the hydrophobic 'tail' and m is a number of oxyethylene groups ($\text{—}OCH_2CH_2\text{—}$) in the surfactant molecule. The oxyethylene groups with a terminal hydroxyl group form a hydrophilic 'head' of molecule. This group of compounds includes monoheptyl ether of pentaethylene glycol (C_7E_5), whose aqueous mixture was investigated in this paper. The specific molecular structure of compounds of this type, related to the presence of hydro- and lipophilic groups, allow them mixing with both polar and nonpolar solvents. Therefore, these are widely used as solvents, co-solvents, surfactants or co-surfactants. These compounds are mostly used in the form of aqueous solutions. Amphiphiles of the C_nE_m type are miscible with water within a limited range of composition and temperature. For practical purposes, it is important to know the miscibility diagram of these systems. Worthy of particular note are two phase phenomena, *i.e.* the appearance of a typical miscibility gap in solution [1–11] and microheterogeneity of the system [3–6, 9–21]. In aqueous solutions of C_nE_m amphiphiles one can mostly observe the occurrence of miscibility gap with the lower critical solution temperature (LCST). Above this temperature, in a solution with a specified composition occurs a phases separation, where one of them is aqueous phase and the other amphiphile-rich. This phenomenon can be also examined using the differential scanning calorimetry. At a phase separation temperature, the differential heat flow recorded during heating the solution rapidly decreases. This is connected with the stability disturbance of the monophase system caused by the occurrence of the second phase. Simultaneously, this is accompanied by an abrupt increase in the system heat capacity. The determination of the phase separation temperature allows defining the range of miscibility gap occurring in the system. In the previously performed investigations on the miscibility of this type of amphiphiles with water [1–12], this approach was successfully used to determine the boundary between single- and diphase system. It was also used in the present study to examine the miscibility gap in the {C_7E_5 + water} system. Here we report data of the miscibility gap over the wide range of concentration which has not been published before. Another phase phenomenon observed in the mixtures under discussion is microimmiscibility connected with the aggregation of amphiphile molecules. For the description of structural changes taking place in diluted aqueous solutions, it is important to determine the conditions of the equilibrium between the isotropic micellar and homogeneous phase in which monomers and small aggregate are present. For this purpose, one can also analyze changes in the third derivative of Gibbs free energy with respect to composition and/or pressure and/or temperature. Such a magnitude is partial molar heat capacity of amphiphile in solution, defined as:

$$C_{p,2} = -T\left(\frac{\partial^3 G}{\partial n_2 \partial^2 T}\right)_{p,n_1} \tag{1}$$

Changes in this quantity are a sensitive indicator of structural changes in solution, resulting from changes in its composition (n_2) and temperature (T). The analysis of $C_{p,2} = f(m_2)$ dependence was

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Table 1
Chemical name, source and purity of investigated amphiphile.

Abbreviation	Chemical name	Supplier	CAS No.	Molar mass/g·mol^{-1}	Mass fraction purity
C_7E_5	Pentaethylene glycol monoheptyl ether, *n*-heptylpentaoxyethylene	Bachem	65316-79-2	336.47	0.99

previously successfully used to describe the aggregation phenomena in {C_nE_m + water} system [3–5, 11–13]. This approach was also used to determine, in the phase diagram, the boundary between homo- and microheterogeneous area in aqueous C_7E_5 mixtures. Moreover, to obtain additional information about the solution structure, the calorimetric data were analyzed from the point of view of two-point scaling theory [10–13, 19–21]. The present paper is the first which describe aggregation process in the {C_7E_5 + water} system. The DSC measurements allowed also for determination of the heat capacity of pure C_7E_5, in rather wide temperature range – the data which has not been published before.

2. Experimental

2.1. Materials

The name, source, CAS number and purity of nonionic amphiphile under investigation are reported in Table 1. Organic compound was used as received without further purification. Water used to prepare all the solutions and as a c_p reference was firstly triple distilled and then degassed by heating under vacuum. Solutions were prepared by weight (Sartorius, RC 210 D type).

2.2. Measurements

In order to study the phase phenomena occurring in aqueous C_7E_5 solutions, we used the differential scanning calorimetry (Micro DSC III Setaram – France). The specific heat capacities were measured using the *continuous with reference* method, in which water was used as the reference substance. A *batch* type cell with a volume of about 1 cm^3 was used. The detailed description of the measurement procedure has been included in our previous study [22]. We measured the specific heat capacities of aqueous C_7E_5 solutions in which the amphiphile mass fraction was $w_2 < 0.12$. Measurements were carried out within the temperature range of (273.15–338.15) with a scanning rate of 0.35 °/min. The recorded curves of the differential heat flow temperature dependences for aqueous C_7E_5 ($0.010 \le w_2 \le 0.702$) solutions were analyzed to determine the range of miscibility gap in the system.

3. Results and discussion

3.1. Miscibility gap

The monoalkyl ether of polyoxyethylene glycol investigated in this study – C_7E_5, mixes with water within a limited range of composition and temperature, forming the miscibility gap with the lower critical solution temperature (LCST). A typical course of the dependence of differential heat flow on temperature, $HF = f(T)$ for one of the solutions examined is shown in Fig. 1.

The appearance of the second phase in solution brings about a stepwise decrease in *HF* that reflects a growth in the heat capacity of solution in this process. For each of the mixtures examined, we determined the temperature of equilibrium transition (T) between the single-phase and two-phase solution, *i.e.*, so-called extrapolated *onset temperature*. The *onset point* is an intersection point of tangent, drawn where the curve has the highest slope, and the extrapolated baseline. For the {C_7E_5 + water} system, we determined the temperature at *onset point* (T) for each of the solutions with various content of amphiphile (w_2). The values of the phase separation temperatures are presented in Table S1 of supplementary materials.

Only a few papers on the mutual miscibility of monoheptyl ether of pentaethylene glycol (C_7E_5) with water could be find in the literature. Much attention is given to C_nE_5 homologues with even number of carbon atoms in the chain. The experimental LCST values of aqueous mixtures of C_6E_5 and C_8E_5 are 75 °C and 60 °C, respectively. Thus, one can expect that the value of LCST for the {C_7E_5 + water} system should be about 68 °C. The value of LCST for the analyzed system, calculated by Garcia-Lisbona et al. [23] from SAFT-HS (statistical associating fluid theory-hard sphere) amounts to 54 °C. Kahlweit et al. [24] have proposed an empirical equation that makes it possible to estimate LCST on the basis of the molecular structure of C_nE_m amphiphile, *i.e.* taking into account the values of n and m in the following form:

$$t^{LCST}_{Kahlweit} = (-1055 + 4285/n) + \frac{1448 - 5152/n}{1 + 1.2m} m \qquad (2)$$

The calculated from Eq. (2) value of the lower critical solution temperature of aqueous C_7E_5 mixtures amounts to 65.71 °C. Sassen et al. [25] have investigated the effect of pressure and the composition of {C_7E_5 + water} system on the temperature at which the second phase appears. These data were compared with our results obtained by the DSC method in the form of $T = f(w_2)$ curve. A miscibility gap with a lower critical solution temperature was obtained (Fig. 2).

Obtained by us and determined on the base of Sassen et al. data, values of lower critical solution temperature (LCST) and critical weight fraction (w_c) of C_7E_5 are presented in table below.

LCST/K	w_c	Data
342.2	0.139	This paper
339.8	0.093	Calculated[a]

[a] On the base Sassen et al. data [25].

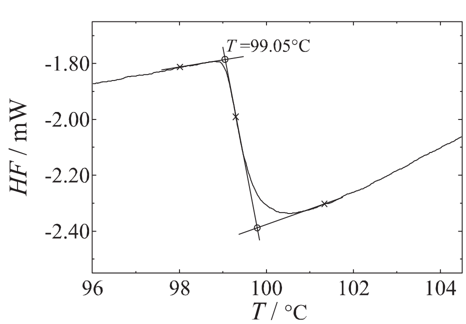

Fig. 1. Typical course of $HF = f(T)$ curve during heating of aqueous solution of C_7E_5 with miscibility gap ($w_2 = 0.7021$) – determination of the phase separation point temperature.

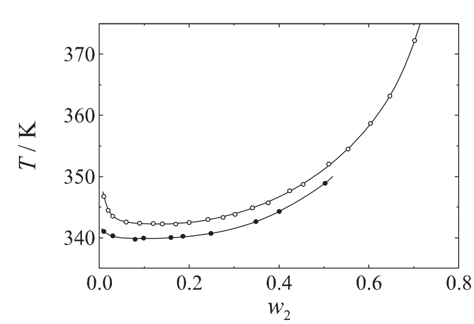

Fig. 2. Miscibility curve of the {C_7E_5 + water} system: ○ – experimental data, ● – ref. [25].