

# Heat capacity and phase behaviour of aqueous 2-(hexyloxytetraethoxy)ethanol by DSC

Henryk Piekarski, Mariola Tkaczyk\*

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

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## Abstract

The specific heat capacities of aqueous solutions of 2-(hexyloxytetraethoxy)ethanol ( $C_6E_5$ ) have been measured from 283 to 338 K within the whole composition range by DSC. Changes of specific, partial and apparent molar heat capacities of investigated system were analysed and considered as a effect of structural transformations. For each solution, the temperature dependences of the differential heat flow were also analysed in order to find the curve of phase coexistence, i.e. the boundary between one- and two-phase area for the examined system.

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*Keywords:* Heat capacity; Coexistence curve; 2-(Hexyloxytetraethoxy)ethanol; Water; DSC

## 1. Introduction

Critical phenomena taking place in aqueous solutions of non-ionic surfactants have been recently the subject of numerous studies. The present paper concerns aqueous solutions of 2-(hexyloxytetraethoxy)ethanol ( $C_6E_5$ ). This compound belongs to poly(ethylene glycol) monoalkyl ethers represented by the general formula:  $\{C_nH_{2n+1}(OCH_2CH_2)_mOH\}$ , included also among short-chain non-ionic surfactant. In aqueous solutions of these compounds, one can observe a typical miscibility gap as well as microheterogeneous areas. These areas are connected with the formation of molecular and micellar aggregates. Amphiphiles, among which  $C_6E_5$  is included, form usually globular micelles in dilute aqueous solutions [1–3]. Assuming their globular shape, Paduano et al. [2] has determined the radius of  $C_6E_5$  micelle (1.72 nm) that is formed in a solution whose concentration is given as the critical micelle concentration (CMC) at a temperature of 298 K. Under these conditions, the aggregation number does not exceed  $N=25$  [1,3,4]. At 298 K, the value of

CMC cited in the literature amounts to: 109 mM (spectrofluorometry [5]), 103 mM (density [5]), 94 mM (ultrasonic absorption [5]), 117 mM (self-diffusion [1]), 107 or 130 mM (calorimetry [4]), depending on the measuring method used.

One of the possible methods for the determination of miscibility diagrams is the analysis of the behaviour of third derivatives of the excess Gibbs free energy versus composition and/or pressure and/or temperature. The diagrams obtained by this method set out boundaries between regions, which are characterized by different molecular organizations, and especially between homogeneous and microheterogeneous areas. In the case of systems, which tend to form metastable molecular and micellar aggregates, one can often observe anomalies in the course of apparent and excess partial molar: heat capacity [6–9], volume [6–9], thermal expansivity [6–10] and mixing enthalpy [11–13], caused by a change in the composition of solution. These functions reach extreme values or show inflection points, especially in the water-rich region of mixture composition. Such a behaviour of the above mentioned data suggests the existence of association similar to that appearing during micellarization, involving also surfactants [6,14]. A source

\* Corresponding author. Tel.: +48 42 6355817; fax: +48 42 6355814.  
E-mail address: [martka@uni.lodz.pl](mailto:martka@uni.lodz.pl) (M. Tkaczyk).

of information about the phenomena of aggregation taking place in solutions can be, among others, changes in the partial molar heat capacity ( $C_{p,2}$ ) that as the third mixed derivative of free energy is given by the following equation:

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

The aim of the present work is to analyse the changes in the partial and apparent molar heat capacity of 2-(hexyloxytetraethoxy)ethanol in aqueous solutions, as a function of temperature and the composition of mixture. For that purpose, the specific heat capacity ( $c_p$ ) of the  $C_6E_5$ /water mixtures were measured within the temperature range from 283 to 338 K within the whole composition range by differential scanning calorimetry. The measured  $c_p$  values were used to calculate the molar heat capacities ( $C_p$ ) of the amphiphile–water mixtures as well as the partial ( $C_{p,2}$ ) and apparent molar heat capacities ( $C_{\phi,2}$ ) of 2-(hexyloxytetraethoxy)ethanol in the examined solutions at several temperatures. For each mixture, the temperature dependence of the differential heat flow (HF) was also analysed in order to find the curve of phase coexistence for the  $C_6E_5$ /water system under investigation and the boundary between the one-phase and two-phase area.

## 2. Experimental

2-(Hexyloxytetraethoxy)ethanol  $\{C_6H_{13}O(CH_2CH_2O)_5H\}(C_6E_5)$  was a Bachem product with declared purity better than 99%. It was used without further purification. Deionised water was triply distilled in an argon atmosphere and degassed. The purity of water was checked by conductometry; the specific conductivity was less than  $2 \times 10^{-6} \text{ S cm}^{-1}$  at 298 K. All solutions were prepared by weighting and then degassed by ultrasound just before the experiment. The specific heat capacities under a constant pressure of  $C_6E_5$ /water mixtures were measured by means of a high sensitivity differential scanning calorimeter based on Tian–Calvet's idea (type Micro DSC III, Setaram, France). The 'continuous with reference' method was used. Within the examined temperature range (283–338 K), the temperature was changed at a constant rate of 0.15 K/min. The measuring vessel was a standard 'batch' type cell with a volume of about  $1.0 \text{ cm}^3$ . A Sartorius RC 210D balance (with an accuracy of  $2 \times 10^{-5} \text{ g}$ ) was used to determine the sample mass. Water was used as a reference liquid. The uncertainty of the  $c_p$  measurements with a Micro DSC III is  $\pm 0.15\%$ , excluding the effects of sample impurities. The details of apparatus and measuring procedure are described elsewhere [15].

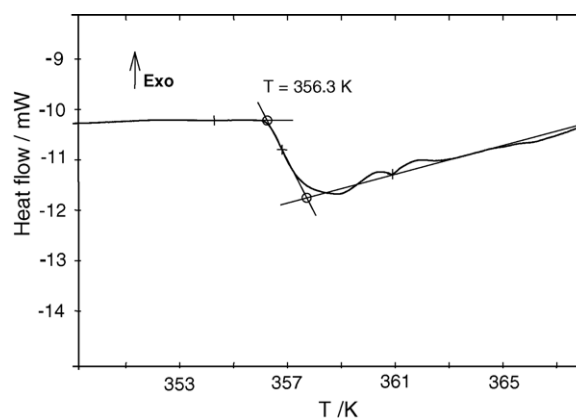


Fig. 1. A DSC trace of aqueous 2-(hexyloxytetraethoxy)ethanol (the mole fraction of amphiphile  $x_2 = 0.04518$ ).

## 3. Results and discussion

### 3.1. Miscibility gap in $C_6E_5$ /water system

The examined 2-(hexyloxytetraethoxy)ethanol belongs to a group of compounds, which form with water a system possessing a miscibility gap with a lower critical solution temperature (LCST). Papers concerning the phase behaviour of the discussed system quote a value of LCST near 348 K [16,17]. However, there is no data showing a relation between the composition of solution and the temperature, at which the second phase appears. In order to provide more complete description of the phase separation in the system under investigation, we analysed the course of temperature relationships of the differential heat flow (HF) obtained by DSC. The examined solutions contained from about 5 to 63wt.% ( $0.003 < x_2 < 0.09$ ) of the surfactant. The course of a typical curve recorded between 323 and 368 K at a scanning rate of  $0.1^\circ/\text{min}$  is shown in Fig. 1.

The heat flow in the temperature range, where the single-phase solution is stable, shows a higher value than that within the range of two-phase system. The appearance of the second phase in solution brings about a stepwise decrease in HF that reflects a drop in the heat capacity of solution in this process. In the case of solutions with  $x_2 < 0.003$ , no characteristic leap in the curve  $HF = f(T)$  was observed due to too low difference between the heat capacities of the single-phase and two-phase system. For each of the examined  $C_6E_5$ /water mixtures we have 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 base line.

In Fig. 2, the curve  $T = f(x_2)$  shows the effect of the amphiphile content in solution on the transition temperature between the single-phase and two-phase solution. No results could be found in the literature for comparison.

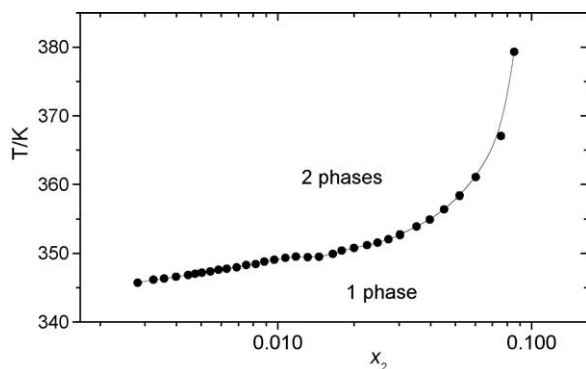


Fig. 2. Coexistence curve for C<sub>6</sub>E<sub>5</sub>/water mixtures.

### 3.2. Heat capacity

The molecular interpretation of heat capacity is not easy. However, the analysis of its changes brought about by variable composition and/or temperature may be helpful in the observation of structural changes taking place in solution. In the case of systems, which tend to form metastable molecular and micellar aggregates, one can observe characteristic changes in the course of excess molar, partial and apparent molar heat capacities.

The determined in this work specific heat capacities of each mixture within the examined temperature range are described by the polynomial:

$$c_p(T) = \sum_{i=-1}^3 A_i T^i \quad (2)$$

where  $c_p(T)$  is the specific heat capacity of the examined solution at temperature  $T$  (K) and  $A_i$  the constant.

The selection of the polynomial degree ( $i$ ) depends of the shape of the experimental curve  $c_p = f(T)$  obtained for the mixture with precisely defined composition. The interpolated values of  $c_p$  at seven selected temperatures are given in Table 1.

The dependence of the specific heat capacity of the C<sub>6</sub>E<sub>5</sub>/water system on the composition at several temperatures is shown in Fig. 3.

The curves  $c_p = f(x_2)$  for  $x_2 > 0.01$  have similar character, therefore for better clarity, Fig. 3a shows only two of them for extreme temperatures. At temperatures from 318 to 338 K, the curves  $c_p = f(x_2)$  show a monotonic drop in the values of specific heat capacities with the increase in the amphiphile content within the whole range of mixture composition. Significant differences in the shape of  $c_p = f(x_2)$  function, for temperature from 283 to 308 K, can be observed only in dilute solutions (Fig. 3b). The specific heat capacities initially decrease slightly, while within the composition range:  $0.002 \leq x_2 \leq 0.0035$  one can observe their increase up to maximum value. A decrease in temperature causes the maximum to grow and appear in the solution with a higher content of the amphiphile. Thus, one may believe that in dilute solutions and at temperatures lower than 318 K, the increase in

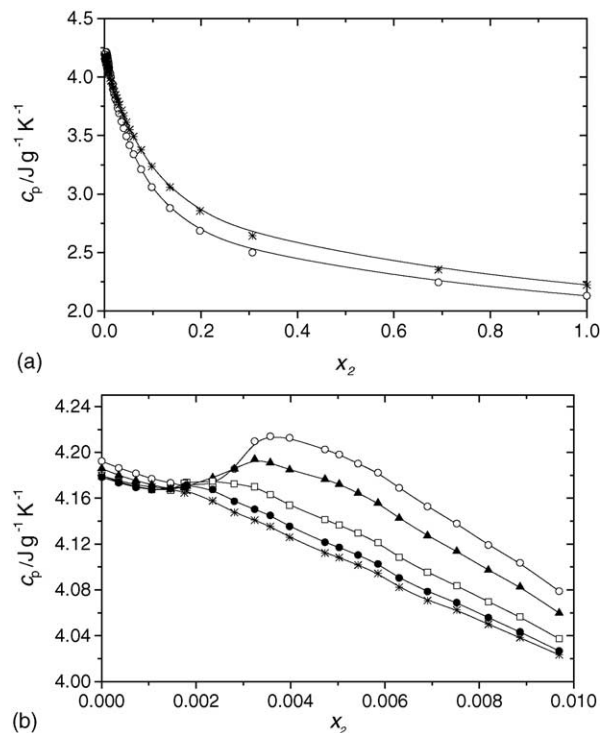


Fig. 3. The specific heat capacities ( $c_p$ ) of aqueous solutions of C<sub>6</sub>E<sub>5</sub> against the mole fraction of amphiphile at various temperatures: (a) (○) 283 K; (\*) 338 K; (b) (○) 283 K; (▲) 288 K; (□) 298 K; (●) 308 K; (\*) 338 K.

the C<sub>6</sub>E<sub>5</sub> content in solution considerably changes the structure of solution. At higher temperatures, these changes are insignificant and result from gradual addition of amphiphile molecules to already existing aggregates.

On the base of experimentally determined specific heat capacities data, using general thermodynamic relationships, we have calculated molar heat capacities ( $C_p$ ), and excess molar heat capacities ( $C_p^E$ ) of solutions as well as:

- apparent molar heat capacity ( $C_{\Phi,2}$ ) of amphiphile:

$$C_{\Phi,2} = M_2 c_p + 1000 \frac{c_p - c_{p,1}^*}{m_2} \quad (3)$$

- partial molar heat capacities ( $C_{p,2}$ ) of amphiphile (C<sub>6</sub>E<sub>5</sub>) in mixtures with water:

$$C_{p,2} = C_{\Phi,2} + m_2 \left( \frac{\partial C_{\Phi,2}}{\partial m_2} \right)_{T,p} \quad (4)$$

where  $M_2$  is the solute molecular weight;  $m_2$  the molality;  $c_p$  and  $c_{p,1}^*$  the specific heat capacity of solution and pure water, respectively.

Excess molar functions are often used to describe the thermodynamic properties of liquid two-component mixtures. The sign and shape of these functions provide information about intermolecular interactions and the structure of solutions. The changes in the excess molar heat capacity ( $C_p^E$ ) of the C<sub>6</sub>E<sub>5</sub>/water mixture brought about by the change in its composition and temperature are shown in Fig. 4.

Table 1  
Specific heat capacity,  $c_p$ , of 2-(hexyloxytetraethoxy)ethanol ( $x_2$ ,  $m_2$ )/water mixtures from 283 to 338 K

$x_2$	$m_2$ (mol kg <sup>-1</sup> )	$c_p$ (J g <sup>-1</sup> K <sup>-1</sup> )						
		283 K	288 K	298 K	308 K	318 K	328 K	338 K
0	0	4.1924	4.1859	4.1798	4.1784	4.1796	4.1826	4.1870
0.00036	0.01996	4.1864	4.1800	4.1742	4.1735	4.1754	4.1804	4.1849
0.00072	0.04017	4.1816	4.1753	4.1703	4.1695	4.1717	4.1758	4.1807
0.00106	0.05900	4.1769	4.1717	4.1677	4.1675	4.1697	4.1734	4.1773
0.00146	0.08118	4.1734	4.1679	4.1669	4.1684	4.1683	4.1675	4.1689
0.00175	0.10065	4.1705	4.1693	4.1733	4.1702	4.1646	4.1613	4.1619
0.00180	0.10012	4.1726	4.1705	4.1737	4.1716	4.1668	4.1633	4.1639
0.00235	0.13075	4.1710	4.1778	4.1750	4.1676	4.1577	4.1541	4.1550
0.00281	0.15629	4.1855	4.1856	4.1726	4.1573	4.1476	4.1447	4.1475
0.00324	0.18066	4.2097	4.1975	4.1700	4.1504	4.1409	4.1380	4.1369
0.00357	0.19861	4.1946	4.1862	4.1632	4.1450	4.1354	4.1320	4.1353
0.00398	0.22155	4.2127	4.1848	4.1492	4.1314	4.1237	4.1218	4.1230
0.00473	0.26382	4.2026	4.1766	4.1413	4.1216	4.1123	4.1094	4.1104
0.00503	0.28082	4.1981	4.1723	4.1365	4.1171	4.1084	4.1050	4.1056
0.00543	0.30293	4.1902	4.1645	4.1296	4.1105	4.1017	4.0984	4.0963
0.00585	0.32677	4.1823	4.1558	4.1212	4.1027	4.0944	4.0913	4.0922
0.00630	0.35204	4.1691	4.1427	4.1085	4.0905	4.0823	4.0793	4.0798
0.00690	0.38555	4.1528	4.1274	4.0954	4.0785	4.0707	4.0676	4.0680
0.00752	0.42049	4.1379	4.1137	4.0836	4.0689	4.0625	4.0596	4.0613
0.00819	0.45845	4.1192	4.0973	4.0697	4.0558	4.0500	4.0483	4.0500
0.00886	0.49643	4.1037	4.0827	4.0565	4.0434	4.0383	4.0365	4.0386
0.00969	0.54320	4.0788	4.0598	4.0373	4.0267	4.0233	4.0245	4.0287
0.01180	0.66266	4.0303	4.0155	3.9972	3.9896	3.9875	3.9889	3.9903
0.01312	0.73799	3.9985	3.9868	3.9736	3.9679	3.9665	3.9673	3.9695
0.01647	0.92926	3.9376	3.9329	3.9293	3.9288	3.9302	3.9331	3.9272
0.01786	1.0092	3.8989	3.8968	3.8954	3.8971	3.9010	3.9060	3.9111
0.01996	1.1306	3.8578	3.8592	3.8631	3.8675	3.8710	3.8731	3.8734
0.02247	1.2757	3.8112	3.8157	3.8238	3.8319	3.8391	3.8441	3.8457
0.02471	1.4062	3.7935	3.8005	3.8205	3.8390	3.8553	3.8696	3.8200
0.02729	1.5572	3.7342	3.7441	3.7608	3.7730	3.7815	3.7869	3.7917
0.03030	1.7344	3.6899	3.7035	3.7254	3.7409	3.7516	3.7586	3.7638
0.03518	2.0240	3.6198	3.6373	3.6647	3.6845	3.6985	3.7078	3.7137
0.03970	2.2948	3.5627	3.5823	3.6134	3.6359	3.6521	3.6622	3.6702
0.04518	2.6263	3.4943	3.5157	3.5502	3.5758	3.5939	3.6052	3.6142
0.05201	3.0456	3.4173	3.4412	3.4788	3.5061	3.5265	3.5413	3.5513
0.06018	3.5546	3.3406	3.3669	3.4081	3.4395	3.4634	3.4835	3.4918
0.07563	4.5416	3.2108	3.2363	3.2789	3.3133	3.3407	3.3616	3.3763
0.09777	6.0153	3.0589	3.0825	3.1251	3.1616	3.1920	3.2167	3.2355
0.13562	8.7093	2.8797	2.9001	2.9390	2.9750	3.0074	3.0359	3.0600
0.19782	13.689	2.6852	2.7020	2.7342	2.7667	2.7986	2.8287	2.8556
0.30664	24.548	2.5001	2.5114	2.5354	2.5619	2.5898	2.6175	2.6433
0.69244	124.97	2.2453	2.2523	2.2725	2.2927	2.3140	2.3367	2.3541
1		2.1305	2.1375	2.1522	2.1678	2.1862	2.2058	2.2236

For each of the considered temperatures, the curves  $C_p^E = f(x_2)$  have the same character. The values of  $C_p^E$  are positive within the whole composition range, thus the molar heat capacities of the examined solutions are higher than the sum of the contributions of pure components. The relationships  $C_p^E = f(x_2)$  pass through a broad maximum, whose shape and position are independent of temperature, although its height increases with temperature. Quantitative and qualitative changes in  $C_p^E$  in the pre-micellar region ( $x_2 < 0.00175$ , i.e.  $m_2 < 0.100$  mol/kg) are very similar and practically independent of temperature. However, after exceeding CMC one can observe differences in the shape of  $C_p^E = f(x_2)$  curves,

which seem to be due to the formation of associates with different thermal stabilities.

A valuable information on the pseudomicrophase transitions taking place in water-rich solutions of amphiphile can be drawn out from the observation of changes in the apparent and/or partial molar heat capacity. Figs. 5 and 6 show the apparent and partial molar heat capacities of  $C_{6E5}$  in aqueous solutions, as a function of temperature and composition.

Figs. 5a and 6a present the changes in  $C_{\phi,2}$  and  $C_{p,2}$  within the large composition range and at a temperature of 283 K (at the remaining temperatures the character of changes is similar). Figs. 5b and 6b show the curves of

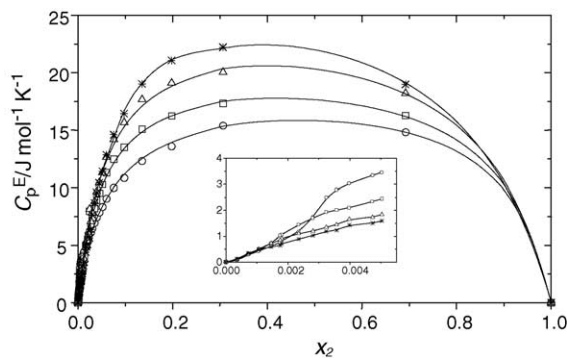
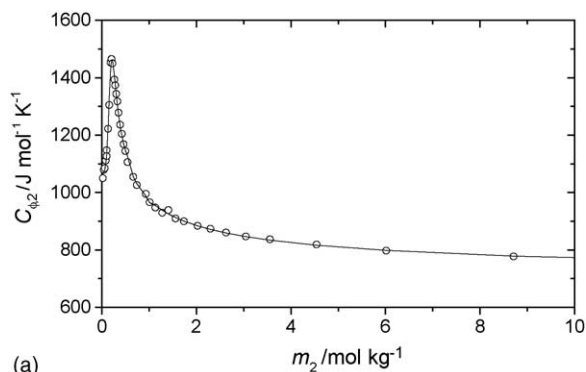
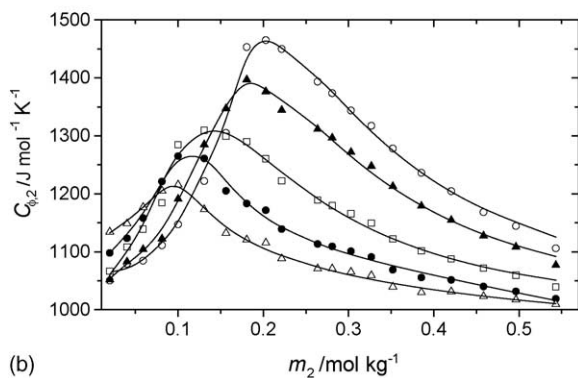


Fig. 4. Molar excess heat capacities ( $C_p^E$ ) of  $\text{C}_6\text{E}_5$ /water mixtures vs. the mole fraction of amphiphile as a function of temperature: (○) 283 K; (□) 298 K; (△) 318 K; (\*) 338 K.

$C_{\phi,2} = f(m_2)$  and  $C_{p,2} = f(m_2)$ , respectively, for dilute solutions ( $m_2 < 0.54 \text{ mol/kg}$ ) at temperatures from 283 to 318 K. Under these conditions, both the apparent and partial molar heat capacities of  $\text{C}_6\text{E}_5$  reach the maximum value. The height of the maximum for both quantities under discussion is the greatest at 283 K and it is lowered with increasing temperature. The increase in temperature shifts the maximum to compositions with higher water contents. After reaching maximum values, both  $C_{\phi,2}$  and  $C_{p,2}$  begin to decrease sharply with the increase in the solution molality. The negative slopes of  $C_{\phi,2} = f(m_2)$  and  $C_{p,2} = f(m_2)$  decrease considerably for so-

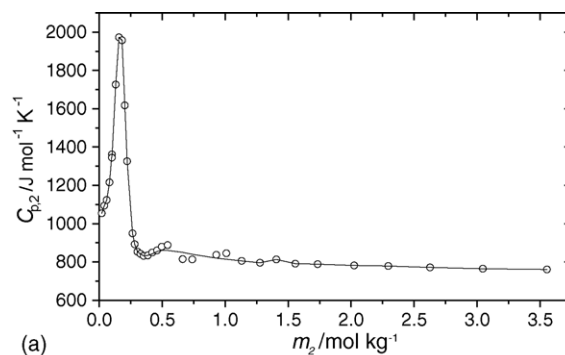


(a)

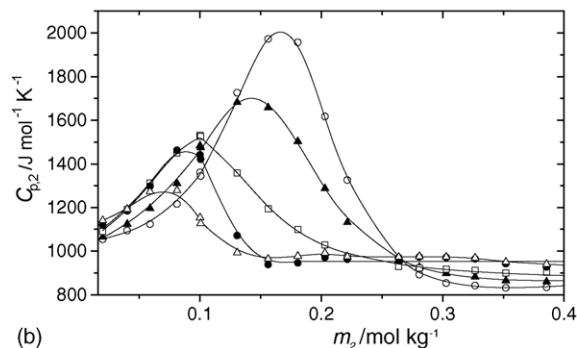


(b)

Fig. 5. Apparent molar heat capacities ( $C_{\phi,2}$ ) of  $\text{C}_6\text{E}_5$  in the amphiphile/water mixtures at various temperatures: (a) (○) 283 K; (b) (○) 283 K; (▲) 288 K; (□) 298 K; (●) 308 K; (△) 318 K.



(a)



(b)

Fig. 6. Partial molar heat capacities ( $C_{p,2}$ ) of  $\text{C}_6\text{E}_5$  in the amphiphile/water mixtures at various temperatures: (a) (○) 283 K; (b) (○) 283 K; (▲) 288 K; (□) 298 K; (●) 308 K; (△) 318 K.

lutions containing more than 0.3 mol of  $\text{C}_6\text{E}_5$  in 1 kg of water (Figs. 5a and 6a). There is no maximum at temperatures of 328 and 338 K.

Distinct changes in the shape of the  $C_{\phi,2} = f(m_2)$  and  $C_{p,2} = f(m_2)$  functions under the influence of changing temperature and composition of solution result certainly from structural transformations of the examined system. The formation of hydration shell around the  $\text{C}_6\text{E}_5$  molecule is connected with the competition of hydration of polar groups and hydrophobic hydration of hexyl chains. The formation of intermolecular hydrogen bonds between the etheral oxygen atoms (and hydroxyl group) of amphiphile and water molecules reinforces their reorientation and weakens the primary water structure. This effect is however compensated by the hydrophobic properties of the hydrocarbon chain [18]. The phenomenon of hydrophobic hydration provoke the reinforcement of the hydrogen bond network between water molecules in water-rich mixtures [18,19]. The phenomena under discussion are affected by temperature as well as the concentration of amphiphile in water. The increase in its content causes the changes in solution structure; formation of the self-associates of amphiphile in solution causes the micellization and microheterogeneity of the system. The drop in temperature or lowering the kinetic energy of molecules causes this process to proceed with more distinct changes in the heat capacity as confirmed by the increased heights of the extremums of the  $C_{\phi,2} = f(m_2)$  and  $C_{p,2} = f(m_2)$  functions observed in Figs. 5b and 6b. Qualitatively similar character of the dependence of  $C_{\phi,2}$  and  $C_{p,2}$  on composi-



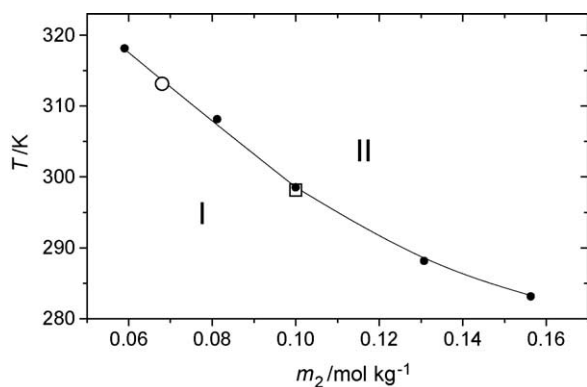


Fig. 7. The mixing scheme boundary separating regions I and II in aqueous solution  $C_6E_5$ : (I) domination of monomers and small associates; (II) globular micelles and large aggregates; (●) the maximum of partial molar heat capacity (this paper); (○) CMC value [5]; (□) CMC value [4].

tion was also observed in the case of the 2-butoxyethanol ( $C_4E_1$ )–water system [20]. This was the basis to divide the whole region of compositions of this mixture into various ranges, depending on the structural changes taking place in solution.

The process of incorporation of amphiphile molecules into micelles is diffusion-controlled and its polydispersibility is low [5]. According to Ortona et al [4], the micellarization of short-chain amphiphiles should be perceived through a prism of changes in water structure due to the hydrophobic interactions between the hydrocarbon ‘tails’ of surfactant molecules. These interactions result in such a self-organisation of surfactant molecules that facilitates subsequent micellarization. On the other hand, the interactions between oxyethylene groups have a limited extent and they require a considerable reorganization of solvent molecules, playing a minor part in the process of micelle formation.

The relation between the composition of  $C_6E_5$ /water, for which the  $C_{p,2} = f(m_2)$  function reaches its maximum, and temperature is shown in Fig. 7.

In our opinion, the obtained curve is a boundary between the area where the surfactant molecules occur as monomers or small aggregates and the region (of composition and temperature), in which first micellar aggregates appear. In the case of many aqueous solutions of non-electrolytes, the appearance of non-miscibility ‘microregions’, even at the temperature  $30^\circ$  below the lower critical solution temperature (LCST), is a not seldom observed phenomenon. The formation of clathrate-like structures and micellar aggregates is a significant factor affecting the appearance of microheterogeneity. At a temperature of 298 K, the maximum of partial molar heat capacity of amphiphile ( $C_{p,2}$ ) appears in the solution containing 0,100 mol of  $C_6E_5$  in 1 kg of water. The value obtained by us is in good agreement with the previously cited literature data concerning the critical concentration of micellarisation. Also the value of CMC at a temperature of 313 K,

obtained by Frindi et al. [5], 68 mM, is well located in the curve shown in Fig. 7.

### 3.3. Conclusion

The phase diagram of {2-(hexyloxytetraethoxy)ethanol + water} system was determined by a sensitive DSC technique. Two boundaries have been drawn: (i) between single and two-phase area (miscibility gap); (ii) between region where the amphiphile molecules occur as monomers or small aggregates and the area in which first micelles appear. For the determination of (i), we have used the fact that the appearance of the second phase in solution brings about a stepwise decrease in the differential heat flow that reflects a drop in the heat capacity of solution in this process. In order to draw (ii) boundaries, behaviour of the third derivative of the excess Gibbs free energy versus composition and temperature (partial molar heat capacity) was analysed. Results of our investigations confirm the usefulness of DSC measurements for determinations of miscibility diagrams.

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