

HEAT CAPACITY OF AQUEOUS 2-(2-HEXYLOXYETHOXY)ETHANOL SOLUTIONS BY DSC

Application of two-point scaling to pseudophases coexistence

H. Piekarski*, M. Tkaczyk and M. Wasiak

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

The specific heat capacities of aqueous solutions of 2-(hexyloxyethoxy)ethanol (C_6E_2) have been measured from 2 to 55°C within the whole available composition range by DSC. Changes of specific, partial and apparent molar heat capacities of investigated system were analysed and considered as an effect of structural transformations. The two-point scaling theory was applied to the description of the binary mixtures properties in the pseudophases coexistence region.

Keywords: DSC, heat capacity, 2-(2-hexyloxyethoxy)ethanol, water

Introduction

Homologous series of non-ionic surfactants being monoalkyl derivatives of polyoxyethylene glycol with a general formula $\{C_nH_{2n+1}(OCH_2CH_2)_mOH\}$, have been frequently studied in consideration of their numerous applications in the industry and basic research. In aqueous solutions of these compounds a typical miscibility gap as well as microheterogeneous areas frequently appear. These areas are connected with the formation of molecular and micellar aggregates. The present paper concerns aqueous solutions of 2-(2-hexyloxyethoxy)ethanol (abbreviated to C_6E_2). Also in this system the appearance of miscibility gap and a phenomenon of microheterogeneity is observed. The determined by Lai *et al.* [1] lower critical solution temperature (LCST) is $T_c=283.94$ K (10.8°C) and the critical mass fraction $\omega_c=0.112$, while the same parameters cited by Lim *et al.* [2] amount to 284 K (11°C) and 0.130, respectively. The upper critical solution temperature (UCST), estimated on the basis of the statistical associating fluid theory (SAFT), is about 500 K (227°C) [3]. The width of the miscibility gap depends on temperature and, for instance, at a temperature of 303.15 K (30°C) it appears for $0.02 < \omega_2 < 0.60$ [2], where ω_2 – mass fraction of C_6E_2 in the aqueous mixtures.

One of the possible methods for the determination of miscibility diagrams is the analysis of the behaviour of the derivatives of the excess Gibbs free energy vs. composition and/or pressure and/or temperature. The diagrams obtained by this method set out boundaries between regions, which are characterised by different molecular organizations, and especially

between homogeneous and microheterogeneous areas. The partial molar heat capacity ($C_{p,2}$) as the third derivative of Gibbs energy,

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

is particularly sensitive to structural changes taking place in solution. Hence, an analysis of the heat capacity as a function of the solution concentration and of temperature should give us important information about the phenomena of aggregation taking place in solutions.

The aim of the present work is to analyse the changes in the partial and apparent molar heat capacity of 2-(2-hexyloxyethoxy)ethanol in aqueous solutions, as a function of temperature and composition of mixture. For that purpose the specific heat capacity (c_p) of the C_6E_2 /water mixtures were measured within the temperature range from 2 to 55°C within the whole composition range by differential scanning calorimetry, which is an effective technique for the determination of thermal behaviour of compounds [4, 5]. 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-(2-hexyloxyethoxy)ethanol in the examined solutions at several temperatures. To analyse the changes in the partial and apparent molar heat capacities we used also the so-called two-point scaling model [6, 7]. The conventional scaling approach is usually applied when the phase transition is considered in respect of temperature, which is a leading variable. The method can be also used when the phase transition or the coexistence of phases depends on the other variable, for instance, the molality of so-

* Author for correspondence: kchfpiek@uni.lodz.pl

lution. This approach has been already successfully used to describe the phenomena of aggregation in the systems: C₄E₁/water system [6] and decyltrimethylammonium bromide/water [7].

Experimental

2-(2-hexyloxyethoxy)ethanol {C₆H₁₃O(CH₂CH₂O)₂H} (C₆E₂) was a Fluka product with declared purity better than 98%. The substance was dried with activated in vacuum at $T=570$ K for more than 24 h molecular

Table 1 Specific heat capacity c_p , of 2-(hexyloxyethoxy)ethanol (m_2)/water mixtures from 2 to 55°C

$m_2/\text{mol kg}^{-1}$	$c_p/\text{J g}^{-1} \text{K}^{-1}$						
	2°C	5°C	10°C	15°C	25°C	40°C	55°C
0.0	4.2077	4.1990	4.1887	4.1821	4.1757	4.1742	4.1775
0.02795	4.2171	4.2081	4.1965	4.1885	4.1813	4.1774	4.1817
0.04383	4.2184	4.2094	4.1979	4.1899	4.1763	4.1789	4.1839
0.08332	4.2189	4.2098	4.1966				
0.10794	4.2230	4.2140	4.2016				
0.14477	4.2515	4.2390	4.2173				
0.19251	4.2983	4.2782	4.2389				
0.25507	4.3098	4.2804	4.2404				
0.36731	4.2765	4.2483	4.2125				
0.50632	4.2250	4.2044	4.1702			miscibility gap	
0.75569	4.1512	4.1329	4.0923				
1.0603	4.0734	4.0567	4.0337				
1.0752	4.0655	4.0503	4.0272				
1.2054	4.0134	4.0000	3.9840				
1.5272	3.9538	3.9425	3.9254				
1.6299	3.9409	3.9299	3.9145				
2.4736	3.7720	3.7679	3.7625				
2.7763	3.7185	3.7161	3.7139				
3.2454	3.6437	3.6443	3.6445	3.6506			
3.4322	3.6132	3.6149	3.6163	3.6230			
4.0121	3.5255	3.5386	3.5593	3.5789			
4.3992	3.4839	3.4897	3.4974	3.5057			
4.7393	3.4417	3.4487	3.4583	3.4679			
5.3339	3.3773	3.3857	3.3974	3.4083			
5.7978	3.3293	3.3390	3.3528	3.3655	3.3957		
6.1456	3.3010	3.3114	3.3265	3.3404	3.3713		
7.5581	3.1791	3.1915	3.2104	3.2279	3.2602		
9.1243	3.0782	3.0921	3.1135	3.1333	3.1694		
10.643	2.9969	3.0115	3.0343	3.0555	3.0941	3.1480	
11.815	2.9433	2.9584	2.9819	3.0038	3.0437	3.0989	
13.159	2.8874	2.9026	2.9265	2.9490	2.9908	3.0488	
23.503	2.6455	2.6597	2.6829	2.7057	2.7498	2.8135	2.8757
35.697	2.5091	2.5219	2.5432	2.5646	2.6077	2.6731	2.7392
54.102	2.4124	2.4237	2.4428	2.4622	2.5018	2.5632	2.6272
75.919	2.3566	2.3674	2.3857	2.4043	2.4424	2.5007	2.5591
117.52	2.2955	2.3049	2.3210	2.3378	2.3727	2.4278	2.4841
195.27	2.2480	2.2568	2.2718	2.2872	2.3193	2.3695	2.4206
397.50	2.2036	2.2121	2.2265	2.2414	2.2721	2.3192	2.3660
pure C ₆ E ₂	2.1627	2.1701	2.1829	2.1964	2.2246	2.2684	2.3112

sieves type 4 Å (from Lancaster) and purified prior to use, by fractional distillation (boiling point: 124°C at 13 hPa). The purity of C₆E₂ checked by gas-liquid chromatography (GLC) was >99.5% by mass. The water content, determined by the Karl-Fisher method was less than 0.2 mass%. Water used as a standard was deionized and then triply distilled in an argon atmosphere and degassed. The purity of water was checked by conductometry; the specific conductivity was less than 2·10⁻⁶ S cm⁻¹ at 25°C. All solutions were prepared by mass and then degassed by ultrasound just before the experiment. The specific heat capacities under a constant pressure of C₆E₂/water mixtures were measured by means of a high sensitivity Tian-Calvet type differential scanning calorimeter (Micro DSC III, Setaram, France). The 'continuous with reference' method was used. Within the examined temperature range (2–55°C) the temperature was changed at a constant rate of 0.15 K min⁻¹. The measuring vessel was a standard 'batch' type cell with a volume of about 1.0 cm³. A Sartorius RC 210D balance (with an accuracy of 2·10⁻⁵ 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 ±0.15%, excluding the effects of sample impurities. The details of apparatus and measuring procedure are described elsewhere [8].

Due to the miscibility gap in the C₆E₂/water system the heat capacities were measured within the whole composition range only at temperatures from 2 to 10°C. At higher temperatures the measurements were limited to the mutual solubility area of the system.

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

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

where *c_p*(*T*) – specific heat capacity of the examined solution at temperature *T*; *A_i* – constant.

The selection of the polynomial degree (*i*) depends of the shape of the experimental curve *c_p*=*f*(*T*) obtained for each particular mixture with precisely defined composition. The interpolated values of *c_p* at seven selected temperatures are given in Table 1 (no data – miscibility gap).

The molar heat capacity, *C_p* = 412.9 J mol⁻¹ K⁻¹, of pure C₆E₂ at a temperature 5°C, calculated in this work from the *c_p* data, agrees quite well with the value estimated from group additivity by Douheret and co-workers (410 J mol⁻¹ K⁻¹) [9].

Results and discussion

Heat capacity

The dependence of the specific heat capacity of the C₆E₂/water system on the composition within the whole composition range at temperature 2°C is shown in Fig. 1a. The analogous curves for two other examined temperatures below the lower critical solution temperature (i.e. 5 and 10°C) exhibit very similar shape. It is characterized by a maximum in the water-rich range and sharp decrease of the function beyond the maximum. The negative slope of the function within this area becomes smaller along with the increase of the amphiphile content. Within the range of diluted aqueous solutions, below 0.1 mol kg⁻¹ (Fig. 1b), at 2, 5 and 10°C the specific heat capacities practically do not depend on the solution composition within the measurements error limits. The further increase in the amphiphile content in the mixture brings about a considerable increase in *c_p* to reach the mentioned earlier maximum. The maximum is the highest at 2°C and it systematically decreases with increasing temperature. No change in the position of this extremum with the temperature was observed probably due to the relatively narrow temperature range available for these measurements. It is worthwhile to mention that our studies on aqueous solutions of C₄E₁ [6] and C₆E₅ [10] indicated that the maximum of *c_p* in these systems changes its position only when the temperature grows significantly.

The apparent molar heat capacities, *C_{φ,2}* and partial molar heat capacities *C_{p,2}* of C₆E₂ in the mixtures with water were calculated according to formulas:

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

$$C_{p,2} = C_{\phi,2} + m_2 (\partial C_{\phi,2} / \partial m_2)_{T,p} \quad (4)$$

where: *M₂* (g mol⁻¹) is the amphiphile molecular mass; *m₂* (mol kg⁻¹) is the molality; *c_p* and *c_{p,1}^{*}* (J g⁻¹ K⁻¹) is the specific heat capacity of solution and pure water, respectively.

The calculated values of *C_{φ,2}* and *C_{p,2}* are given in Table 2. The dependence of the partial molar heat capacity of C₆E₂ in aqueous solutions on the solution molality within the wide range of composition at temperature 2°C is shown in Fig. 2a. The shape of the above function at the temperature 5 and 10°C is similar. The same dependence, within the range of dilute solutions (*m₂* < 0.5 mol kg⁻¹) at temperatures: 2, 5 and 10°C is presented in Fig. 2b. The examined function for C₆E₂ in water exhibit a distinct maximum in the range of high water content in the system which decreases when the temperature increases. The effect of the temperature change on the maximum position was not observed here due to a narrow range of examined

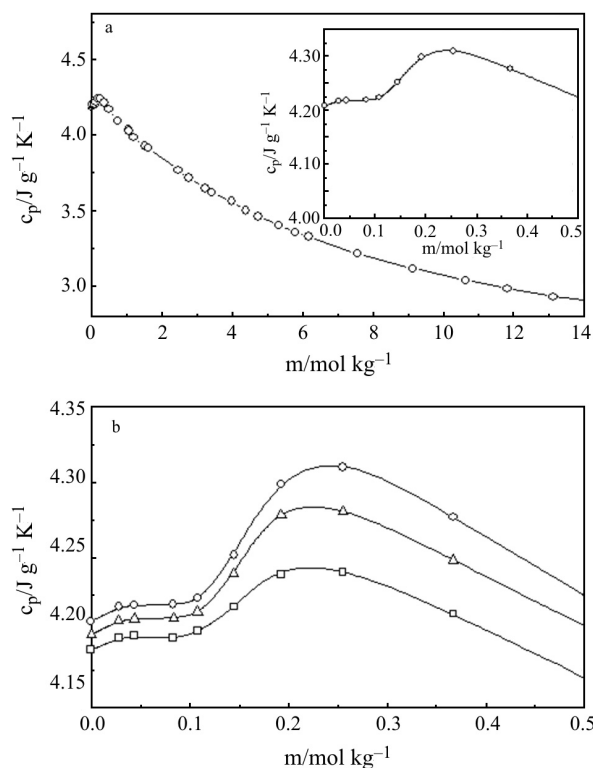


Fig. 1 The specific heat capacities (c_p) of C_6E_2 /water mixtures vs. the molality of solution at various temperatures: a) \circ – 2°C; b) \circ – 2°C; \triangle – 5°C; \square – 10°C

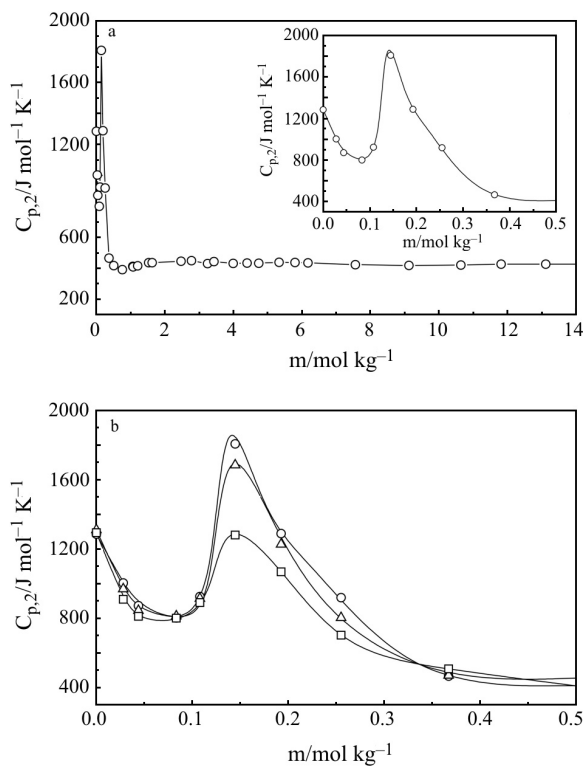


Fig. 2 Partial molar heat capacities ($C_{p,2}$) of C_6E_2 in the amphiphile/water mixtures at various temperatures: a) \circ – 2°C; b) \circ – 2°C; \triangle – 5°C; \square – 10°C

temperature. Beyond the maximum, the $C_{p,2}$ function decreases along with the increasing concentration. Similar courses of the dependences under discussion were observed by us previously for aqueous solutions of 2-butoxyethanol (C_4E_1) [6] and 2-(hexyloxytetraethoxy)ethanol (C_6E_5) [10] within a relatively wide temperature range (LCST (C_4E_1) \cong 49°C; LCST (C_6E_5) \cong 75°C). Generally, these characteristic changes in the course of partial molar heat capacities as a function of the composition are observed in liquid systems which tend to form metastable micellar or pseudomicellar aggregates [11–16]. The same concerns the $C_{\phi,2}=f(m_2)$ function. Therefore, it can be supposed that in examined here system C_6E_2 /water the analogous phenomenon appears.

It is generally assumed that in a micellar system the position of the $C_{p,2}=f(m_2)$ maximum corresponds to the critical micelle concentration cmc . Analogously, in the systems which exhibit pseudophase behavior, like C_4E_1 /water the position of the $C_{p,2}$ function maximum determines a boundary separating region of homogenous solution and micelle-like dispersed phase at given temperature [6]. The latter opinion was confirmed in our earlier work on C_4E_1 /water system in which the $C_{p,2}$ maximum positions as a function of temperature agreed very well with the experimentally determined critical molality values reported in Westh *et al.* paper [17].

The position of the $C_{p,2}$ function maximum at 5°C, determined in this work $m_{max}=0.145$ mol kg^{-1} agrees very well with the value of cmc at the same temperature obtained by Douheret *et al.* on the base of analysis of volumetric properties of the C_6E_2 /water system that is $m_c=0.15$ mol kg^{-1} ($x_2=0.0027$) [9]. The cited authors noted that there was a very strong similarity between the shape of the excess molar volumes plot for the C_6E_2 /water system and that for C_6E_3 /water (micelle-forming amphiphile [18]) and concluded that C_6E_2 like C_6E_3 is capable of micelle formation.

In our earlier work [6] we presented opinion that formation of micellar or micelle-like aggregates in solution at given temperature is not the sharp jump nature. There exists an interval of molalities around the critical molality where a variety of structural forms (e.g. molecular clusters or pre-micellar structures) can appear. In order to describe this phenomenon we proposed a new model for analysis of the C_p function in the mentioned above systems which has been derived from the two-point scaling theory [6, 19]. The two-point scaling model was applied successfully for description of the partial molar heat capacity of 2-butoxyethanol [6] and of decyltrimethylammonium bromide in water solution [7].

Two-point scaling relations, fitting procedure and results

The two-point scaling model describes a mixture which can appear in two phases confined by two sta-

bility points of the molality m_p and m_f . In our case the m_p denotes the stability point for lower limit of the concentration of a phase of micellar structure (phase 2) and m_f denotes the stability point for upper limit of the concentration of a phase of homogenous

Table 2 Apparent and partial molar heat capacity ($C_{\phi,2}$ and $C_{p,2}$ in [$\text{J mol}^{-1} \text{K}^{-1}$]) of 2-(hexyloxyethoxy)ethanol (m_2) in aqueous solutions

$m_2/\text{mol kg}^{-1}$	2°C		5°C		10°C	
	$C_{\phi,2}$	$C_{p,2}$	$C_{\phi,2}$	$C_{p,2}$	$C_{\phi,2}$	$C_{p,2}$
0.0	1285.3	1285.3	1310.1	1310.1	1294.3	1294.3
0.02795	1140.5	1003.1	1125.8	968.07	1079.2	908.34
0.04383	1046.2	871.89	1037.4	842.94	1008.5	810.35
0.08332	936.91	800.60	930.63	810.81	893.02	800.02
0.10794	924.98	924.98	912.60	912.60	919.08	890.00
0.14477	1111.6	1807.5	1082.9	1685.0	999.49	1280.0
0.19251	1288.8	1288.8	1225.7	1225.7	1067.2	1067.3
0.25507	1220.2	918.27	1133.7	802.05	1009.8	700.94
0.36731	1001.1	465.42	942.60	469.85	866.32	507.47
0.50632	838.21	417.58	810.73	453.01	757.06	409.16
0.75569	715.20	390.65	699.01	447.87	651.13	418.08
1.0603	648.45	412.17	637.79	423.75	621.35	528.32
1.0752	641.37	409.23	632.39	422.18	616.19	522.57
1.2054	602.50	415.55	596.08	427.65	588.36	490.42
1.5272	586.11	506.49	582.24	510.74	574.57	472.46
1.6299	586.24	503.64	582.71	508.64	576.65	475.15
2.4736	541.65	446.00	542.73	458.23	543.67	482.96
2.7763	531.40	436.00	533.21	449.61	535.69	481.77
3.2454	519.56	429.72	522.53	445.16	525.82	468.24
3.4322	514.34	443.08	517.68	444.43	521.40	462.80
4.0121	500.83	431.79	508.77	453.21	520.42	460.26
4.3993	498.44	433.18	502.82	445.76	508.37	448.50
4.7393	493.30	432.87	497.92	440.11	503.97	445.25
5.3339	486.97	438.39	491.79	433.92	498.12	456.29
5.7978	482.03	437.46	487.04	430.25	493.83	450.55
6.1456	480.61	435.25	485.69	430.34	492.71	448.58
7.5581	468.86	422.48	473.99	428.64	481.49	435.89
9.1243	461.97	418.58	467.07	423.75	474.64	431.23
10.643	456.50	420.14	461.47	423.86	468.93	431.44
11.815	453.08	430.92	457.94	434.33	465.28	439.93
13.159	449.12	437.07	453.81	428.92	460.97	434.21
23.503	436.95	439.80	440.62	415.58	446.47	419.11
35.697	429.87	415.24	432.90	429.60	437.85	419.70
54.102	425.86	415.84	428.39	419.29	432.57	420.00
75.919	424.06	418.34	426.36	417.23	430.22	423.81
117.52	420.55	412.67	422.48	414.46	425.78	417.81
195.27	417.74	407.70	419.50	409.20	422.48	415.31
397.50	414.28	409.91	415.93	411.04	418.75	436.31
pure C ₆ E ₂	411.53	411.53	412.94	412.94	415.39	415.39

structure (phase 1). The stability points are defined by the stability condition which should be satisfied together with the equation of state in their usual meaning in thermodynamics. In the present model they determine the region of phase coexistence [6, 7].

The expressions for the partial molar heat capacity of the amphiphile in each phase derived on the base of the model have the following forms:

for phase 1 (homogenous phase):

$$C_{p,2}^{(s=1)} = C_{p,2}^{01} \left(1 - \frac{m}{m_f}\right)^{-\alpha_1} \quad (5)$$

and for phase 2 (micellar phase):

$$C_{p,2}^{(s=2)} = C_{p,2}^{02} \left(\frac{m}{m_p} - 1\right)^{-\alpha_2} \quad (6)$$

In these formulas α_1 is the critical exponent for $m \leq m_f$, and α_2 for $m \geq m_p$, while $C_{p,2}^{01} = C_{p,2}^{s=1}$ ($m=0$) and $C_{p,2}^{02}$ ($m=2m_p$) are the constants to be determined in the fitting procedure [6, 7]. The crossing point of the two above functions determines the critical molality m_c which corresponds to the *cmc* value.

In terms of the two-point scaling model we were able to describe also the behaviour of $C_{\Phi,2}$ using the known formula (Eq. 4).

The obtained expressions have the form:

$$C_{\Phi,2}(m \leq m_f) = C_{p,2}^{01} \frac{1}{1 - \alpha_1} \frac{m_f}{m} \left[q_0^f - \left(1 - \frac{m}{m_f}\right)^{1-\alpha_1} \right] \quad (7)$$

$$C_{\Phi,2}(m \geq m_p) = C_{p,2}^{02} \frac{1}{1 - \alpha_2} \frac{m_p}{m} \left[q_0^p + \left(\frac{m}{m_p} - 1\right)^{1-\alpha_2} \right] \quad (8)$$

where q_0^f and q_0^p are the constants.

Finally, the derivatives can be calculated:

$$\frac{dC_{\Phi,2}}{dm}(m \leq m_f) = C_{p,2}^{01} \frac{1}{1 - \alpha_1} \frac{m_f}{m^2} \left[-q_0^f + \left(1 - \frac{m}{m_f} + (1 - \alpha_1) \frac{m}{m_f}\right) \left(1 - \frac{m}{m_f}\right)^{-\alpha_1} \right] \quad (9)$$

$$\frac{dC_{\Phi,2}}{dm}(m \geq m_p) = C_{p,2}^{02} \frac{1}{1 - \alpha_2} \frac{m_p}{m^2} \left[-q_0^p - \left(\frac{m}{m_p} - 1 - (1 - \alpha_2) \frac{m}{m_p}\right) \left(\frac{m}{m_p} - 1\right)^{-\alpha_2} \right] \quad (10)$$

The relations given by Eqs (5, 6) and Eqs (7–10) compared with experimental data allow to determine, α_1 , α_2 , m_f , m_p , $C_{p,2}^{01}$ and $C_{p,2}^{02}$ by means of the best fit procedure. The parameters q_0^f and q_0^p select one of the curves $C_{\Phi,2}$ and their derivatives $dC_{\Phi,2}/dm$ from the family defined by other parameters and described by Eqs (7–10) at given temperature. Fitting all three functions simultaneously provides the self-consistent set of the fitting parameters. The details of procedure for the two-point scaling calculations in the case of the heat capacity were described previously [6, 7]. The fitting was controlled, in the first place, by the best fit of the apparent molar heat capacity because this function is directly determined from experiment. The partial molar heat capacity can contain the error resulting from the procedure of differentiation. The results of the best fitting procedure applied to our experimental data within the C_6E_2 molality range from $m_2=0$ to $m_2=1.2$ mol kg⁻¹ are presented in Figs 3–5. The values of critical exponents α_1 , α_2 , stability points m_f , m_p , constants $C_{p,2}^{01}$, $C_{p,2}^{02}$ and the critical molality m_c are collected in Table 3. The values of q_0^f and q_0^p resulting from the best fitting procedure applied to the functions $C_{p,2}$ and $dC_{p,2}/dm$ are given in Table 4.

As it can be seen from presented results the two-point scaling model describes very well the behaviour of C_p functions for aqueous solutions of 2-(2-hexyloxyethoxy)ethanol similarly as it was found previously in the case of aqueous solutions of 2-butoxyethanol [6] and decyltrimethylammonium bromide [7]. The observed phase transition occurs within molality interval from m_f to m_p . This region can be considered as a phase coexistence area. In that case the molality m_c corresponding to the crossing point in Figs 3–5 can be assumed as a boundary between the composition range in which the solution exhibits predominant properties characteristic for homogenous systems ($m < m_c$) and the composition range in which the solution properties becomes typical for heterogenous systems ($m > m_c$). The value of m_c determined on the base of discussed model amounts to 0.159 mol kg⁻¹ (Table 3), which is very close to the mentioned earlier *cmc* value (0.15 mol kg⁻¹) reported in the paper of Douheret *et al.* [9] that characterises the phase transition in 'classical' approach. The values of the stability limits of concentration m_f and m_p and the m_c concentrations do not change within the examined range of temperature. This is probably due to the

Table 3 The values of the critical exponents α_1 , α_2 , stability points m_f , m_p , constants $C_{p,2}^{01}$, $C_{p,2}^{02}$ and the critical molality m_c of the considered systems

$T/^\circ\text{C}$	α_1	α_2	$m_f/\text{mol kg}^{-1}$	$m_p/\text{mol kg}^{-1}$	$C_{p,2}^{01}/\text{J mol}^{-1} \text{K}^{-1}$	$C_{p,2}^{02}/\text{J mol}^{-1} \text{K}^{-1}$	$m_c/\text{mol kg}^{-1}$
2	0.125	0.33	0.16	0.15	810	690	0.1596
5	0.125	0.33	0.16	0.15	800	680	0.1596
10	0.125	0.33	0.16	0.15	778	663	0.1596

rather narrow range of temperature accessible for the calorimetric measurements (value of LCST=284 K).

The critical indices α_1 and α_2 (Table 3) are independent of the temperature, as it was previously observed in the case of 2-butoxyethanol (C_4E_1) aqueous solutions [6], and also their values 0.125 and 0.33, respectively, are the same as in the cited above system. It is noteworthy that in the case of dodecyltrimethylammonium bromide solutions examined earlier with the use of the same model [7], the critical parameters were also temperature independent, but they both α_1 and α_2 assumed the same values, namely 0.125. The results of our most recent studies confirm that for the regular solution (below the m_c molality)

the critical parameter α_1 is always equal to 0.125 [6, 7, 20]. In the case of the solution of spherical micelles the critical index α_2 is also equal to 0.125 [7], while for the molecular clusters it assumes a value of 0.33 [6]. Therefore it can be supposed that examined here aqueous solutions of 2-(2-hexyloxyethoxy)ethanol behave similarly as pseudomicellar 2-butoxyethanol/water mixtures but not as the system in which the typical micelles are formed, what was suggested by other authors [9]. Obviously, this conclusion should be confirmed by determination of the order parameter which can be reflected in the light or neutron scattering experiments.

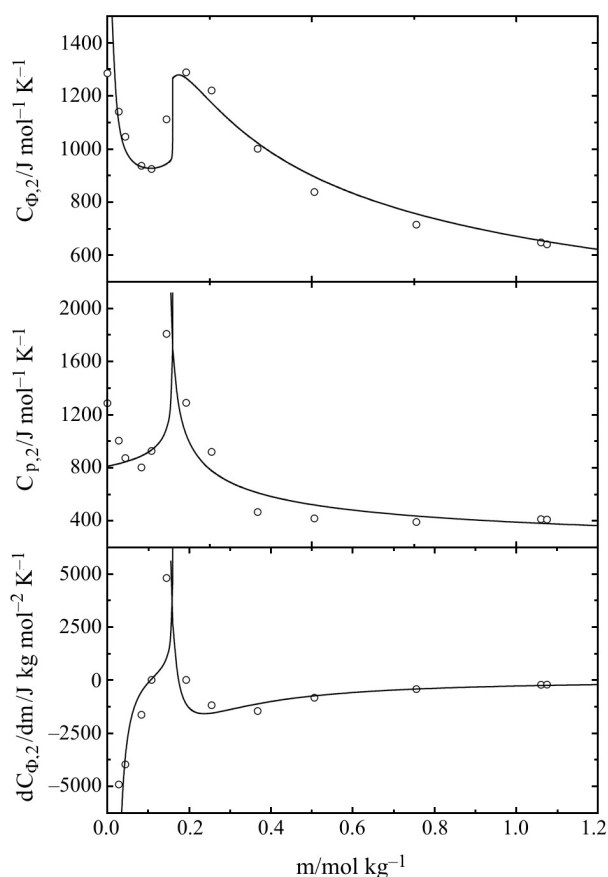


Fig. 3 The phase transition in C_6E_2 described by the power functions predicted in the two-point scaling procedure at 2°C . Circles represents points evaluated from the experimental data according to the Eqs (3) and (4)

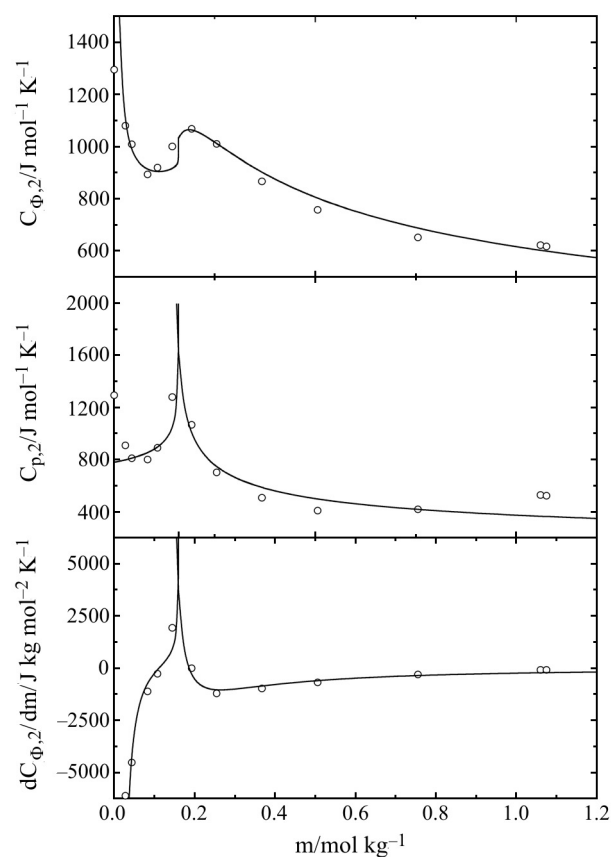


Fig. 4 The phase transition in C_6E_2 described by the power functions predicted in the two-point scaling procedure at 5°C . Circles represents points evaluated from the experimental data according to the Eqs (3) and (4)

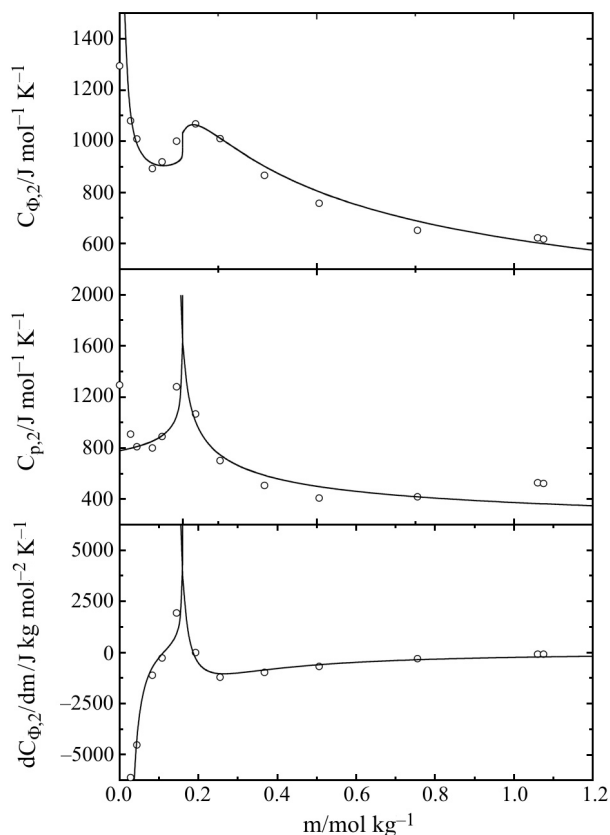


Fig. 5 The phase transition in C_6E_2 described by the power functions predicted in the two-point scaling procedure at 10°C . Circles represents points evaluated from the experimental data according to the Eqs (3) and (4)

Table 4 The values of two fitting parameters q_0^f and q_0^p used for the description of the experimental behaviour of $C_{\Phi,2}$ and $dC_{\Phi,2}/dm$ functions

$T/^\circ\text{C}$	q_0^f	q_0^p
2	1.050	1.150
5	1.055	1.090
10	1.060	0.950

Conclusions

- A course of the apparent and partial molar heat capacity of C_6E_2 in aqueous solution as a function of composition testifies to a presence of phase transitions in the range of high water content.

- The $C_{p,2}$ of the examined system can be successfully analysed within the phase transition area using the two-point scaling model.
- The performed analysis suggests that in the examined here system the phase transition from regular to micelle-like solution takes place.

References

- 1 H.-H. Lai and L.-J. Chen, *J. Chem. Eng. Data*, 44 (1999) 251.
- 2 K.-H. Lim, J. S. Reckley and D. H. Smith, *J. Colloid Interface Sci.*, 161 (1993) 465.
- 3 M. N. Garcia-Lisbona, A. Galindo, G. Jackson and A. N. Burgess, *J. Am. Chem. Soc.*, 120 (1998) 4191.
- 4 F. O. Cedeño, M. M. Prieto, A. Espina and J. R. Garcia, *J. Therm. Anal. Cal.*, 73 (2003) 775.
- 5 J. Datta and A. Balas, *J. Therm. Anal. Cal.*, 74 (2003) 615.
- 6 L. Wojtczak, H. Piekarski, M. Tkaczyk, I. Zasada and T. Rychtelska, *J. Mol. Liquids*, 95 (2002) 229.
- 7 H. Piekarski, M. Tkaczyk, M. Wasiaak, L. Wojtczak, T. Rychtelska and I. Zasada, *accepted for publication in J. Mol. Liquids*, in press.
- 8 P. Góralski, M. Tkaczyk and M. Chorążewski, *J. Chem. Eng. Data*, 48 (2003) 492.
- 9 G. Douhéret, A. H. Roux, M. I. Davis, M. E. Hernandez, H. Høiland and E. Høgseth, *J. Solution Chem.*, 22 (1993) 1041.
- 10 H. Piekarski and M. Tkaczyk, *Thermochim. Acta* 428 (2005) 113
- 11 C. de Visser, G. Perron and J. E. Desnoyers, *Can. J. Chem.*, 55 (1977) 856.
- 12 C. de Visser, G. Perron and J. E. Desnoyers, *J. Am. Chem. Soc.*, 99 (1977) 5894.
- 13 G. Roux, G. Perron and J. E. Desnoyers, *J. Solution Chem.*, 7 (1978) 639.
- 14 J. E. Desnoyers, R. DeLisi and G. Perron, *Pure Appl. Chem.*, 52 (1980) 433.
- 15 G. Roux, D. Roberts, G. Perron and J. E. Desnoyers, *J. Solution Chem.*, 9 (1980) 629.
- 16 G. Perron, J.-F. Côté, D. Lambert, J. Pageau and J. E. Desnoyers, *J. Solution Chem.*, 23 (1994) 121.
- 17 P. Westh, A. Hvidt and Y. Koga, *Chem. Phys. Letters*, 217 (1994) 245.
- 18 S. A. Wiczorek, *J. Chem. Thermodyn.*, 24 (1992) 129.
- 19 L. Wojtczak, *J. Thermal Anal.*, 45 (1995) 639.
- 20 H. Piekarski, *Thermochim. Acta*, 420 (2004) 13.

DOI: 10.1007/s10973-005-6865-7