

## Research Article

# Phase Behavior and Heat Capacity of {DPnP + Water} Mixtures at the Temperature Range of 273.15–338.15 K

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The differential scanning calorimetry method (DSC) was used to examine the miscibility in the {dipropylene glycol propyl ether (DPnP) + water} system. Based on recorded curves of differential heat flow on temperature,  $HF = f(T)$ , the range (composition, temperature) of the occurrence of miscibility gap, the values of lower critical solution temperature (LCST), and critical concentration were determined. On the basis of the experimentally determined specific heat capacity data the partial molar heat capacities ( $C_{p,2}$ ) of DPnP in the mixtures with water were calculated. Analyzing changes in the course of  $C_{p,2} = f(x_2)$  function, the boundary of transition from a homogeneous solution was determined, in which the monomers of amphiphile dominate, to the region, in which aggregates of the cluster type appear.

## 1. Introduction

Monoalkyl ethers of polyoxyalkylene glycols with general formula  $C_nH_{2n+1}[OR]_mOH$  (where  $n$  is number of carbon atoms in hydrocarbon chain of hydrophobic *tail* and  $m$  is number of oxyethylene or oxypropylene groups in hydrophilic *head*) consist a group of nonionic surfactants that exhibit growing importance during the last decades. The generally accepted abbreviations for these amphiphiles are  $C_nE_m$  and  $C_nP_m$ , respectively. On account of their specific properties, these compounds have found a wide use in many fields of life. They were also the subject of numerous experimental investigations. Our previous studies [1] devoted to the derivatives of polyoxyethylene glycols have shown that their molecules in aqueous solution undergo aggregation. Depending on the concentration, temperature, and the alkyl chain length in the nonpolar tail of  $C_nE_m$ , these compounds show different susceptibility to miscibility with water and different values of LCST (lower critical solution temperature) [2–5]. In the 80s of the 20th century, the first reports on the high toxicity of polyoxyethylene amphiphiles ( $C_nE_m$ ) were published. From these reports it followed that the substance tested, used first of all as solvents, exerted an adverse effect on the health and life of men and animals. It has been

found that the metabolism process of amphiphiles  $C_nE_m$  results in the formation of aldehyde and alkoxyacetic acid that can penetrate the cell nucleus causing changes in the genome structure. Therefore  $C_nE_m$  have been included in the list of chemically hazardous substances and up to the end of the 20th century they have been largely replaced with the derivatives of polyoxypropylene glycols ( $C_nP_m$ ), called Dowanol. These are safer for health as their metabolism results in the formation of carbon dioxide that is expelled by lungs. Compared to the polyoxyethylene glycol ethers, these compounds are characterized by a lower inflammability and explosion capability. Owing to the fact that they show a low surface tension and have a great capability to solve hydrophilic and lipophilic compounds, polyoxypropylene glycol ethers are used in various branches of industry such as chemical, cosmetic, pharmaceutical, food, or textile industry. However, despite the growing application importance of Dowanol, there is a lack of fundamental experimental data concerning their thermochemical properties. The amount of experimental data describing phase equilibria in aqueous solutions of the group of  $C_nP_m$  compounds is also limited [6–10]. The above reasons influenced us to undertake the studies of these compounds. The aim of this study is to use differential scanning calorimetry (DSC) to obtain information about the

miscibility of dipropylene glycol propyl ether ( $C_3P_2$  or DPnP) in aqueous solution. The molecules of polyoxyalkylene glycol ethers undergo association in aqueous solutions, which can result in microimmiscibility of system [1, 11–14]. Both of this phenomenon and phase separation in the system, that is, the determination of the range (temperature/composition) of the occurrence of the system miscibility {DPnP + water}, constitute the object of these studies.

## 2. Experiment

**2.1. Materials.** Dipropylene glycol propyl ether,  $C_3H_7[OCH_2CH(CH_3)]_2OH$ , was an Aldrich product with declared purity better than 98.5%. Prior to use the substance was purified by fractional distillation (boiling point: 349.15 K at 8 mmHg) and dried with molecular sieves type 4 Å (from Lancaster) activated in vacuum at 570 K for 48 h. Deionized water was triply distilled in an argon atmosphere and degassed. The purity of water was checked by conductometry; the specific conductivity was less than  $2 \cdot 10^{-6} \text{ S cm}^{-1}$  at 298.15 K. All solutions were prepared by weight with an accuracy of  $2 \cdot 10^{-5} \text{ g}$ .

**2.2. Measurements.** The specific heat capacities under a constant pressure of {DPnP + 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 so-called "continuous with reference" method was used. The heat flow during sample heating with a scanning rate of  $0.35 \text{ K min}^{-1}$  from 273.15 K to 338.15 K was recorded. The specific heat capacity of the mixtures was measured with the use of the "batch" type cell with a volume of about  $1 \text{ cm}^3$ . The details of apparatus and measuring procedure are described elsewhere [15]. The uncertainty of specific heat capacity measurement amounts to about  $\pm 0.2\%$ , excluding the effects of the sample impurities. In order to provide homogeneity at lower temperature than LCST, the solutions were cooled to a temperature about 278 K and placed into a cooled measurement cell and then transferred to a calorimetric block at a temperature of 273.15 K.

To determine the critical miscibility temperature, DSC measurements were performed at a scanning rate of  $R = 0.1 \text{ K} \cdot \text{min}^{-1}$ . No influence of changes in the scanning rate (within  $0.1\text{--}0.5 \text{ K} \cdot \text{min}^{-1}$ ) on the phase separation temperature was found.

## 3. Results and Discussion

**3.1. Miscibility Gap in {DPnP + Water} System.** The examined dipropylene glycol propyl ether forms with water a system exhibiting miscibility gap with LCST. For this reason, at a specified temperature and composition of solution, the phase separation phenomenon occurs. It leads to the appearance of two immiscible phases: water-rich and organic solvent-rich ones. To prepare a phase diagram by DSC method, the differential heat flow (HF) versus temperature was recorded during heating the sample within temperature range of 273.15–338.15 K with a scanning rate of  $0.1 \text{ K min}^{-1}$ . The

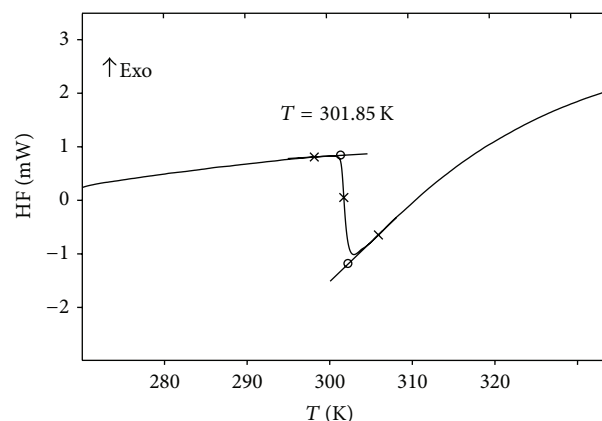


FIGURE 1: A DSC trace of aqueous DPnP (the weight fraction of amphiphile  $w_2 = 0.1560$ ).

studied mixtures contained from about 5 to about 85 mass% DPnP. The trace of typical curve recorded during sample heating is shown in Figure 1.

The heat flow of sample at the temperature, at which the phase separation occurs, suddenly decreases, which is connected with the appearance of endothermic heat effect and a jump-wise increase in the heat capacity of the two-phase system in relation to the one-phase system at the same temperature. The temperature of phase separation was determined as the so-called *onset point*. The *onset point* is an intersection point of tangent drawn where the curve has the highest slope and the extrapolated baseline. Figure 1 shows an example of the  $HF = f(T)$  dependence for the solution, in which the mass fraction of amphiphile  $w_2 \approx 0.156$ . The determined temperature of extrapolated peak beginning amounts to 301.85 K.

For each of the {DPnP + water} mixtures showing a limited miscibility within the investigated temperature range, the transition temperature between the single-phase and two-phase solution was determined. The results obtained are listed in Table 1.

The phase diagram drawn on the basis of the experimental data is presented in Figure 2.

The determined value of LCST for {DPnP + water} system amounts to 287.03 K for a solution with the critical mass fraction  $w_c = 0.468$ . It is worth mentioning here that the DSC method used in this work, compared to phase equilibrium methods, allows relatively quick, precise, and little labor-consuming determination of these values. Additionally, its use makes it possible to determine the course of function  $w_2 = f(T)$  for compositions close to  $w_c$ , for which, for example, the phase volume method is insufficiently effective.

The data obtained by us are well consistent with appropriate literature data obtained by other methods. Investigating the clouding phenomenon of aqueous mixtures of DPnP by turbidity methods, Bauduin et al. [9] obtained the values of LCST amounting to 286.95 K. Estimated from the function  $T = f(w_2)$  presented in their paper, the critical mass fraction amounts to  $w_c = 0.45 \pm 0.05$ . Recently Lin et al. [10], using the phase volume method, determined the value of LCST as

TABLE 1: Equilibrium temperature for {DPnP ( $x_2$ ,  $w_2$ ) + water} system.

$x_2$	$w_2$	$T/K$	$t/^\circ\text{C}$
0.00616	0.05687	336.44	63.29
0.00771	0.07061	327.01	53.86
0.00983	0.08849	318.76	45.61
0.01202	0.10635	312.82	39.67
0.01635	0.13988	304.95	31.80
0.01856	0.15613	301.85	28.70
0.02194	0.17998	298.22	25.07
0.02488	0.19973	295.80	22.65
0.02753	0.21690	294.01	20.86
0.03170	0.24259	291.82	18.67
0.03487	0.26117	290.81	17.66
0.03857	0.28185	289.01	15.86
0.04206	0.30046	288.06	14.91
0.04847	0.33258	287.52	14.37
0.05164	0.34751	287.47	14.32
0.05223	0.35029	287.46	14.31
0.05960	0.38274	287.20	14.05
0.06369	0.39960	287.00	13.85
0.06550	0.40672	287.11	13.96
0.06879	0.41952	287.08	13.93
0.07350	0.43699	287.05	13.90
0.07702	0.44941	287.04	13.89
0.07968	0.45860	287.04	13.89
0.08255	0.46812	287.03	13.88
0.08816	0.48603	287.05	13.90
0.09052	0.49336	287.06	13.91
0.09802	0.51531	287.08	13.93
0.10465	0.53400	287.13	13.98
0.11270	0.55411	287.18	14.03
0.11683	0.56404	287.25	14.10
0.12729	0.58797	287.32	14.17
0.14086	0.61599	287.50	14.35
0.18408	0.68821	289.26	16.11
0.21477	0.72796	292.01	18.86
0.25124	0.76651	295.47	22.32
0.28907	0.79912	300.58	27.43
0.34407	0.83692	311.96	38.81
0.38360	0.85893	327.28	54.13

$x_2$ ,  $w_2$ : mole fraction and mass fraction of DPnP in solution, respectively.

286.59 K and  $w_c = 0.486$ . Also the value of DPnP solubility in water at 298.15 K (17.1 mass %) reported by Bauduin et al. [9] is similar to that obtained by us (18.0 mass %). The presented above literature data concerning miscibility in the system {DPnP + water} are also given in the diagram (Figure 2).

In the group of simple polypropylene glycol monoethers, the extension of molecule by an additional oxypropylene group causes a decrease in the molecule hydrophilicity. This causes a decrease in the value of LCST widening the concentration range of miscibility gap [9]. Therefore the

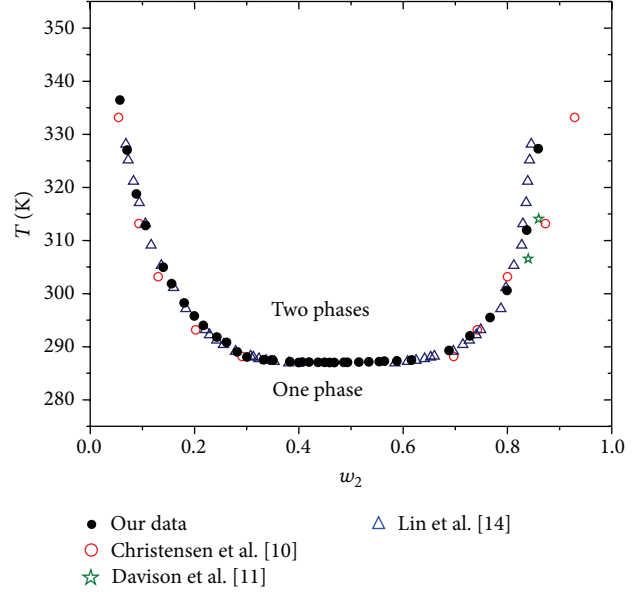


FIGURE 2: Coexistence curve for {DPnP + water} mixtures.

highest value of LCST is shown by propylene glycol propyl ether (305.05 K) for dipropylene glycol propyl ether LCST = 286.95 K, and for tripropylene glycol propyl ether this value only amounts to 278.55 K.

**3.2. Specific Heat Capacity ( $c_p$ ) of {DPnP + Water} System.** Heat capacity under a constant pressure is one of the basic thermodynamic quantities used among others in chemical engineering. The analysis of its changes caused by temperature and the solution composition gives many valuable pieces of information about structural changes occurring in aqueous solutions.

The character of the experimental curve  $c_p = f(T)$  obtained depends on the mixture composition, similarly as it was observed in the systems examined by us earlier. A typical course of this dependence for the completely miscible solution and solution with miscibility gap is presented in Figure 3.

The specific heat capacities of mixtures determined within the examined temperature range (only for one-phase systems) are described by the polynomial:

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

where  $c_p(T)$  is specific heat capacity of solution at temperature  $T$ ;  $A_i$  are constants.

The selection of the polynomial degree ( $i$ ) depends of the shape of the experimental curve obtained for the mixture with a defined composition. The interpolated values of specific heat capacity at ten selected temperatures are given in Table 2 (no data, miscibility gap). A typical course of the dependence  $c_p = f(x_2)$  within the whole examined composition range at 283.15 K is shown in Figure 4.

The curves  $c_p = f(x_2)$  for a wide range of the solution composition were obtained only within the 273.15 to 283.15 K

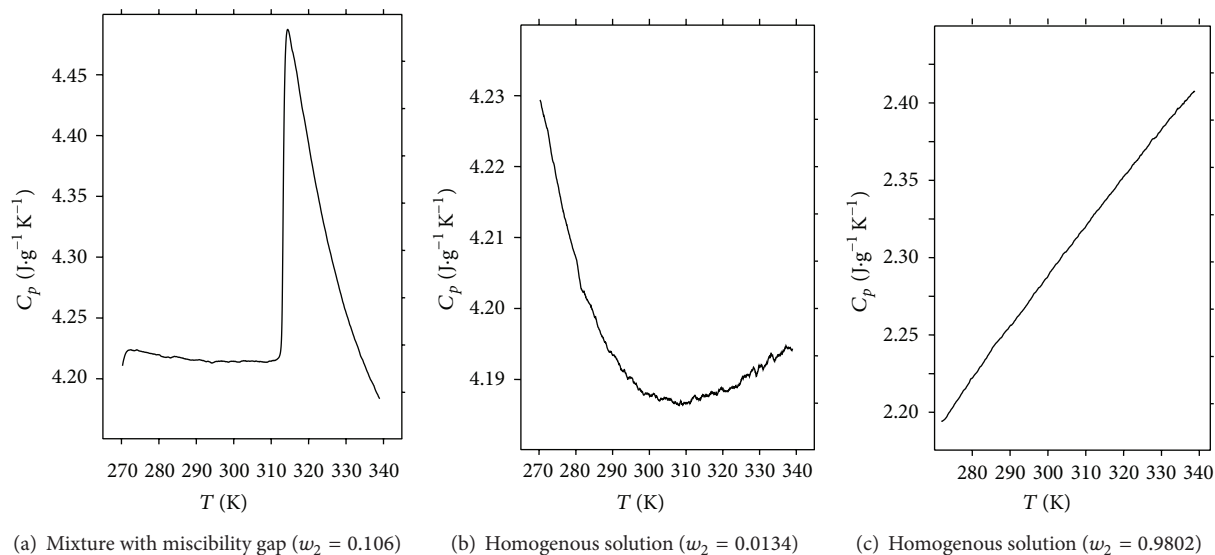


FIGURE 3: Specific heat capacity of some aqueous solutions of DPnP.

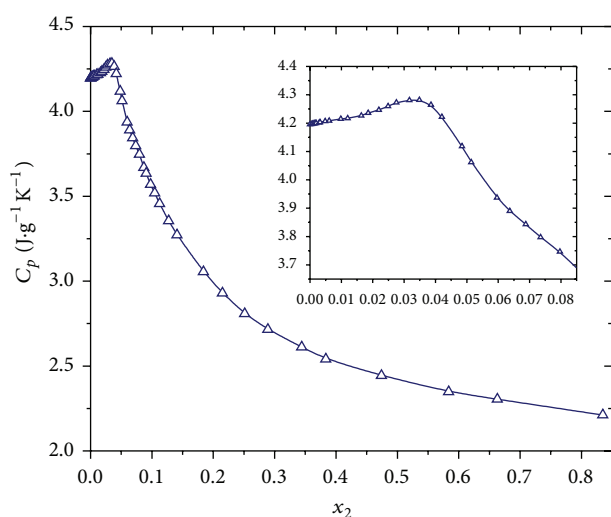
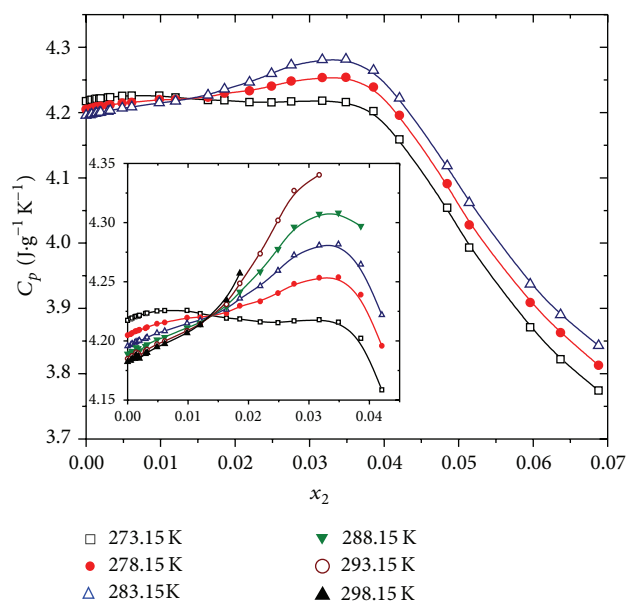


FIGURE 4: Specific heat capacity of {DPnP + water} mixtures versus mole fraction of DPnP at 283.15 K.

temperature range due to the occurrence of miscibility gap at about 287 K. These curves have similar shape characterized by a maximum in the water-rich range and sharp decrease of the function beyond the maximum. The negative slope of  $c_p = f(x_2)$  becomes smaller along with the increase of the amphiphile content. The dependence of the specific heat capacity on the investigated composition for low concentrations of amphiphile at several temperatures is shown in Figure 5.

The increase in temperature makes the maximum of the  $c_p = f(x_2)$  function higher. No change in the position of this extremum with temperature was observed probably due to the relatively narrow temperature range available for these measurements. Our previous studies [1] concerning ether derivatives of polyoxyethylene glycols show that a change

FIGURE 5: Specific heat capacity of the {DPnP ( $x_2$ ) + water} at selected temperatures.

in the position of the maximum mentioned above can be observed only for a wider examined temperature range. The occurrence of the maximum of function  $c_p = f(x_2)$  is probably connected with structural changes occurring in solution due to a change in its composition and temperature, especially with the formation of greater aggregates or micelles [1].

**3.3. Partial Molar Heat Capacity of {DPnP + Water} System.** A sensitive indicator of structural changes in the system is the behavior of the third derivative of Gibbs free enthalpy in relation to composition, pressure, and/or temperature.

TABLE 2: Specific heat capacity ( $c_p$ ) of {DPnP ( $x_2$ ,  $m_2$ ) + water} system from 273.15 to 338.15 K.

$x_2$	$m_2$	Specific heat capacity $c_p/\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$									
		273.15	278.15	283.15	288.15	293.15	298.15	308.15	318.15	328.15	338.15
0	0	4.2174	4.2048	4.1956	4.1891	4.1849	4.1823	4.1807	4.1822	4.1854	4.1899
0.00052	0.02902	4.2187	4.2057	4.1965	4.1899	4.1858	4.1834	4.1820	4.1831	4.1859	4.1903
0.00074	0.04081	4.2193	4.2067	4.1976	4.1914	4.1873	4.1848	4.1827	4.1831	4.1855	4.1906
0.00122	0.06798	4.2204	4.2080	4.1986	4.1910	4.1872	4.1850	4.1836	4.1846	4.1872	4.1915
0.00139	0.07716	4.2207	4.2083	4.1992	4.1945	4.1904	4.1879	4.1863	4.1876	4.1904	4.1942
0.00176	0.09797	4.2210	4.2088	4.1999	4.1937	4.1895	4.1871	4.1855	4.1867	4.1894	4.1933
0.00195	0.10845	4.2216	4.2094	4.2003	4.1915	4.1875	4.1851	4.1835	4.1844	4.1871	4.1918
0.00295	0.16412	4.2231	4.2107	4.2017	4.1956	4.1915	4.1891	4.1875	4.1887	4.1916	4.1963
0.00322	0.17943	4.2235	4.2116	4.2030	4.1969	4.1927	4.1901	4.1880	4.1885	4.1908	4.1951
0.00485	0.27073	4.2253	4.2145	4.2067	4.2011	4.1973	4.1949	4.1929	4.1933	4.1954	4.1993
0.00613	0.34210	4.2257	4.2156	4.2083	4.2032	4.1998	4.1975	4.1953	4.1950	4.1964	4.2004
0.00983	0.55882	4.2258	4.2197	4.2148	4.2112	4.2085	4.2067	4.2054	4.2061		
0.01202	0.67520	4.2230	4.2199	4.2172	4.2152	4.2140	4.2134	4.2140			
0.01635	0.92269	4.2192	4.2232	4.2265	4.2289	4.2309	4.2345				
0.01856	1.0497	4.2186	4.2297	4.2359	4.2415	4.2486	4.2571				
0.02194	1.2453	4.2160	4.2334	4.2464	4.2585	4.2737					
0.02488	1.4161	4.2154	4.2404	4.2594	4.2776	4.3019					
0.02753	1.5715	4.2169	4.2482	4.2725	4.2964	4.3270					
0.03170	1.8173	4.2179	4.2534	4.2808	4.3073	4.3403					
0.03487	2.0056	4.2158	4.2538	4.2817	4.3083						
0.03857	2.2268	4.2022	4.2391	4.2646	4.2971						
0.04206	2.4370	4.1586	4.1958	4.2219	*						
0.04847	2.8273	4.0540	4.0911	4.1184							
0.05142	3.0090	3.9930	4.0280	4.0620							
0.05960	3.5180	3.8710	3.9090	3.9370							
0.06369	3.7762	3.8220	3.8630	3.8900							
0.06879	4.1005	3.7741	3.8128	3.8431							
0.07350	4.4038	3.7280	3.7660	3.7975							
0.07968	4.8060	3.6753	3.7127	3.7467							
0.08686	5.2800	3.5987	3.6357	3.6690							
0.09052	5.5250	3.5639	3.6013	3.6350							
0.09802	6.0320	3.4971	3.5350	3.5690							
0.10465	6.4878	3.4465	3.4845	3.5195							
0.11270	7.0507	3.3836	3.4209	3.4558							
0.12729	8.0964	3.2842	3.3207	3.3547							
0.14086	9.1014	3.2003	3.2370	3.2722							
0.18408	12.524	2.9773	3.0161	3.0548	3.0971						
0.21477	15.183	2.8575	2.8942	2.9290	2.9627						
0.25124	18.626	2.7403	2.7748	2.8073	2.8382	2.8682					
0.28907	22.571	2.6503	2.6835	2.7148	2.7446	2.7729	2.8000				
0.34407	29.117	2.5505	2.5817	2.6117	2.6406	2.6686	2.6956	2.7471			
0.38360	34.545	2.4816	2.5118	2.5410	2.5691	2.5964	2.6228	2.6737	2.7224		
0.47428	50.077	2.3883	2.4162	2.4435	2.4703	2.4966	2.5224	2.5724	2.6202	2.6660	2.7097
0.58375	77.845	2.2973	2.3229	2.3481	2.3728	2.3971	2.4210	2.4674	2.5120	2.5548	2.5959
0.66293	109.17	2.2560	2.2803	2.3041	2.3275	2.3505	2.3732	2.4171	2.4595	2.5002	2.5393
0.83504	280.99	2.1703	2.1910	2.2115	2.2316	2.2515	2.2711	2.3095	2.3468	2.3830	2.4181

\* Miscibility gap.

 $x_2$ ,  $m_2$ : mole fraction of DPnP and molality of solution, respectively.



Particularly the observation of changes in the partial molar heat capacity of solute ( $C_{p,2}$ ) that is the third derivative of Gibbs energy in relation to composition and temperature

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

makes it possible to observe changes occurring in the mixture.

The appearance of extrema in the curves of  $C_{p,2} = f(x_2)$  describing the aqueous solutions of amphiphile can indicate the existence of association processes that result in the formation of molecular aggregates with higher thermodynamic stability in solution.

The studies on aqueous solutions of polyoxyethylene glycol ethers have shown that in this type of systems the function  $C_{p,2} = f(x_2)$  exhibits the maximum in the water-rich region [1]. It is a symptom of the formation of molecular aggregates leading to the appearance of microheterogeneity in the system. Analyzing the position of the maximum (composition, temperature) in micellar solution, this makes it possible to determine a boundary between the area where monomers dominate and the region connected with the appearance of aggregates, for example, micellar or pseudomicellar aggregates. Previous studies concerning the aqueous solutions of  $C_nE_m$  [1] indicated that the values of critical micelle concentration (CMC) derived from various experimental methods are well located at the borderline obtained by the analysis of the function under discussion. It means that the above conclusion in relation to ether derivatives of polyoxyethylene glycols has found its confirmation in the results obtained by other methods.

On the basis of the specific heat capacity data determined experimentally, the apparent ( $C_{\phi,2}$ ) and partial molar heat capacities ( $C_{p,2}$ ) of DPnP in the mixtures with water were calculated according to the following formulas:

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

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

where  $M_2$  ( $\text{g mol}^{-1}$ ) is the DPnP molecular mass;  $m_2$  ( $\text{mol kg}^{-1}$ ) is the molality;  $c_p$  and  $c_{p,1}^*$  ( $\text{J g}^{-1} \text{K}^{-1}$ ) are the specific heat capacity of solution and pure water, respectively.

The dependence of the partial molar heat capacity of DPnP in aqueous solutions up to  $x_2 = 0.5$  at 273.15 K and within the range of diluted mixtures at 273.15–293.15 K is shown in Figure 6.

As is seen, the addition of a small amount of Dowanol, DPnP ( $x_2 < 0.015$ ), to water causes a slight decrease in its partial molar heat capacity and then increases until the maximum is reached. Its intensity increases with increasing temperature. In the {DPnP + water} system, the light and neutron diffraction studies did not confirm the hypothesis about the existence of micelles in it [9]. A significant hindrance in the process of micellar aggregation can be the

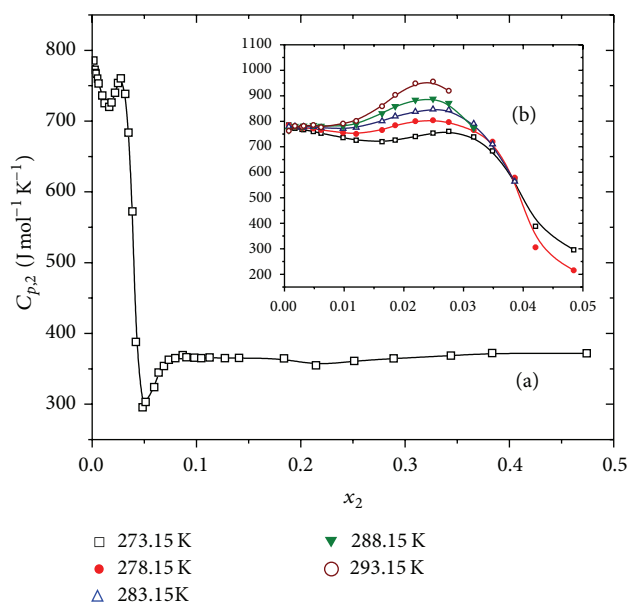


FIGURE 6: Partial molar heat capacity of DPnP in the aqueous solution: (a) up to  $x_2 = 0.5$  at 273.15 K and (b) up to  $x_2 = 0.05$  at 273.15 K, 278.15 K, 283.15 K, 288.15 K, and 293.15 K.

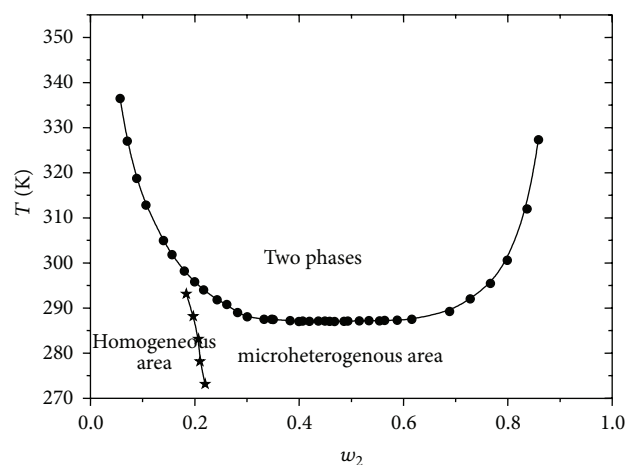


FIGURE 7: The mixing scheme of {DPnP + water} system.

branching of oxypropylene chain. Owing to its structure, the hydrophobic surface of oxypropylene group becomes smaller and simultaneously it constitutes an important hindrance in the H-bond interactions between ether oxygen atom and the hydrogen atoms of water molecules or the hydroxyl proton of other Dowanol molecules. Therefore, the presence of extrema in the course of function  $C_{p,2} = f(x_2)$  should be related to the aggregation of Dowanol molecules in water. However, as a result of this, micelles probably are not formed but rather aggregates of the cluster type are created, whose size and quantitative composition cannot be defined at the present time. Based on the course of function  $C_{p,2} = f(x_2)$  at the given temperature, we determined the composition of solution corresponding to its maximum. The compositions obtained are plotted in the graph shown in Figure 7.

Summarizing, as the result of our studies, we obtained a phase diagram, in which one can observe the following:

- (1) the boundary (composition, temperature) between one-phase and two-phase solutions;
- (2) the area of homogeneous solution where the amphiphile monomers dominate;
- (3) the region where one observes the greater aggregates (clusters), whose presence affects the change in the heat capacity of the system under investigation.

In order to determine the factors that influence the behavior of such systems further investigations on solutions containing Dowanol with different number of oxypropylene groups as well as different length of hydrocarbon chain are necessary. The appropriate studies are underway at the moment.

### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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