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Calorimetry—an important tool in solution chemistry

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Abstract

Calorimetry belongs to the most important experimental techniques. It is the only experimental method allowing for direct measurements of various physical and chemical processes and reactions. When appropriate model is used, analysis of results on molecular level is possible.

This paper is devoted to use of solution calorimetry for investigation of two and three component liquid systems. Special attention is paid on results of dissolution enthalpy and heat capacity measurements. Several ways for analysis of the obtained results are presented. The course of standard enthalpies of solution versus mixed solvent composition can serve as a principal basis of the physico-chemical characteristics of investigated solutions. A quantitative measure of energetic effect of solute–solute interactions in solution can be obtained from analysis of the so-called enthalpic pair interaction coefficients derived from McMillan–Mayer theory. The Mastroianni, Pikal and Lindenbaum "cage model" and model of selective solvation proposed by Covington are useful in discussion of the dissolution enthalpies of hydrophobic solutes in water–organic cosolvent mixtures.

Finally, the application of two-point scaling approach to the description of heat capacity function in microheterogenic systems is presented and discussed.

Keywords: Calorimetry; Dissolution enthalpy; Heat capacity

1. Introduction

The title of this paper is evident for the specialists in the field of calorimetry. However, the rightness of the use of calorimetric methods for investigation of molecular interactions in solutions has been frequently called in question by specialists in other disciplines. Indeed, the heat effect determined calorimetrically is a sum of different energetic effects connected with the examined processes. But when appropriate model of interactions is applied for analysis of these data it is possible, in many cases, to obtain wide information about interesting for us phenomena coming, in fact, from calorimetry. In order to illustrate this view, several models will be presented which have been used for analysis of the results of thermochemical studies carried out in our laboratory. They included the dissolution enthalpies of simple inorganic electrolytes (NaCl, NaI) and some non-electrolytes in water–organic and organic–organic solvent mixtures as well as heat capacities of some two and three-component systems. Why have just these functions been chosen for such studies?

As it is known, the thermodynamic function, which characterizes the total energetic effect of solute–solvent interactions, is the solvation enthalpy, $\Delta_{\mathrm{solv}}H$. This function is connected with the standard dissolution enthalpy of a solid solute, $\Delta_{\mathrm{sol}}H^\circ$ by a simple relation:

$$\Delta_{\mathrm{solv}}H = \Delta_{\mathrm{sol}}H^\circ + H(\text{crystal lattice}) \tag{1}$$

Therefore, in order to discuss a variation of the solvation enthalpy of a chosen solute in different solvents it is sufficient to analyse the standard dissolution enthalpy, as the enthalpy of the crystal lattice is the same in each case. For the description of solutions in binary solvents, a convenient function is the enthalpy of transfer, $\Delta_{\mathrm{tr}}H^\circ$, of the solute from an individual solvent (S) to the mixed solvent (M) of various compositions which can be calculated as a difference of appropriate dissolution enthalpies.

$$\begin{aligned}\Delta_{\mathrm{tr}}H^\circ &= \Delta_{\mathrm{solv}}H^\circ(\mathrm{M}) - \Delta_{\mathrm{solv}}H^\circ(\mathrm{S})\\ &= \Delta_{\mathrm{sol}}H^\circ(\mathrm{M}) - \Delta_{\mathrm{sol}}H^\circ(\mathrm{S})\end{aligned} \tag{2}$$

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Heat capacity at constant pressure is also among important properties of solutions. Being related to the second derivative of the chemical potential with respect to temperature this function is very sensitive to any structural change that occur in the system. For this reason, systematic study of the heat capacity in the mixtures seems to be advisable.

2. Enthalpies of solution and enthalpies of transfer in mixed solvents

It could be expected that, in ideal cases, the dissolution enthalpies of a solute in the binary solvent would be represented by a straight line connecting the $\Delta_{\mathrm{sol}}H^{\circ}$ values in both individual components of the mixed solvent. Such linear or almost linear courses of function $\Delta_{\mathrm{sol}}H^{\circ}$ versus mixed solvent composition were observed only in the systems containing cosolvents with similar properties and whose molecules are of a similar size, shape and structure. Usually, the mentioned above relations deviate from the "linear behaviour" due to the different type interactions among the molecules of both cosolvents leading to the changes of mixture structure with the change of composition, selective solvation, chemical reaction or complex formation in the system etc. Hence, the analysis of the course of the dissolution enthalpy curves can be a source of preliminary information about possible molecular interactions and a structure of the solution. In the "classical approach", the shape of the dissolution enthalpy curves, the positions of extremes or other characteristic points were compared with the run of some functions which illustrated different properties of the mixed solvents. In many cases, it was possible to obtain, in this way, a consistent picture of the examined systems particularly for solutions in water–organic solvent mixtures. As these results published in numerous original papers and some monographs are generally known, they will be recalled only shortly.

The standard dissolution enthalpies of NaI in the mixtures of water with aliphatic alcohols as a function of the mixed solvent composition exhibit maxima at low alkanol content. It is generally accepted that these maxima are related to a structure-promotion or a structure-stabilizing effect of added alkanol on water, due to the hydrophobic hydration of the alcohol alkyl group [1–3]. The position of the $\Delta_{\mathrm{sol}}H^{\circ}$ maximum and, to some extent, its height, depends on the size and the structure of non-polar group of alcohol and for this reason these parameters have been proposed by some authors as a relative measure of the hydrophobicity of the alkanol molecule [4].

It is more difficult to systematise the shapes of the dissolution enthalpy curves of inorganic electrolytes in the mixtures of water with other than alcohols organic solvents. The maxima of the $\Delta_{\mathrm{sol}}H^{\circ}$ have been observed in the mixtures of water with 2-alkoxyethanols (known as cellosolves) [5,6], and with aprotic solvents, such as hexamethylphosphotriamide (HMPA) [7,8], tetrahydrofuran (THF) [9,10], 1, 2-dimethoxyetane (DME) and 2-butanone [11,12]. However, in these systems the maxima of the dissolution enthalpy in the range of high water content are smaller than in the case of alcohols, which contain the same number of carbon atoms in the molecule. The position of the maximum does not shift systematically towards a lower organic cosolvent content, when the size of the non-polar group in the organic solvent molecule increases [4]. Moreover, the height and the position of the maxima depend strongly on the kind of anion of the dissolved salt [4,13]. On the other hand, the dissolution enthalpies of NaI and NaCl in the mixtures of water with *N*,*N*-dimetylformamide (DMF) [14] and dimethylsufoxide (DMSO) [15] run monotonously within the whole range of the mixed solvent composition. The maximum of the $\Delta_{\mathrm{sol}}H^{\circ}$ of electrolytes has not been observed either in the mixtures of water with organic substances, like formamide and urea which do not contain a non-polar group in their molecules [14,16]. It appeared, after detail analysis, that the shape of the $\Delta_{\mathrm{sol}}H^{\circ} = f(x)$ curves in water–organic solvent mixtures, at least in the range of high water content, depends on the organic cosolvent molecule hydrophobicity, understood as a resultant of the hydrophobic effect of non-polar groups and the effect of hydrophilic interactions of functional polar groups present in the molecule [4,6,13]. It is noteworthy, that in the binary solvents in which water has been replaced by an organic solvent, such as methanol or DMF the maxima of the $\Delta_{\mathrm{sol}}H^{\circ}$ do not appear within the range of low cosolvent content [17–20].

An analysis of the shape of dissolution enthalpy curves gives only preliminary information about possible molecular interactions, for instance, about presence or absence of the hydrophobic effects in the examined solution. Therefore, it can serve only as the principal basis for characteristics of investigated solutions. The quantitative evaluation of the energetic effects of interactions is not possible in this way. It seems to be possible if we use for the analysis of calorimetric data the enthalpic pair interaction coefficients model derived from the McMillan–Mayer theory [21]. The enthalpic pair interaction coefficients can be calculated from the enthalpies of dilution (interaction between similar solutes) and the enthalpies of mixing or of dissolution, leading to three-component systems (interaction between dissimilar solutes) [22]. They can be regarded as a measure of the heat effect (i.e. enthalpy of interaction) when two solute particles (the same or different ones) approach each other in dilute solutions. Essentially, the pair interaction coefficients describe the solute–solute interactions. As these interactions are solvent mediated, it should be possible to use the above mentioned coefficients for the analysis of the solute-solvent interactions too.

In a three-component systems containing two solutes X and Y in a solvent S the enthalpic interaction coefficients, h_{XY} illustrate the sum of effects connected with a partial desolvation of both interacting molecules and effects of a different type interaction between particles X and Y. For this reason, it is convenient to analyse the h_{XY} coefficients for a series of pairs consisting of a selected solute X (for instance: NaI) and different solutes Y as, in that case, the variations of the h_{XY} values should depend mostly on the differences in the solvation effects of solute Y and in the effects of direct interaction between X and Y. It have been found that the enthalpic pair interaction coefficients for the pairs of NaI with different non-electrolytes in water are linearly correlated with some properties of the non-electrolytes, such as molecular polarizability (α), reciprocal of the electric permittivity ($1/\varepsilon$) or Dimroth–Reichardt polarity parameter (E_T) [1]. However, these correlations are not general and hold only for groups of related compounds. The best linear correlation, which encompasses almost all systems investigated so far was obtained between the h_{XY} for NaI–non-electrolyte pairs in water and the molar heat capacity of hydration of the non-electrolyte Y [1], and even better with the heat capacity of interactions, $C_p(\text{int})$ between the non-electrolyte Y and solvent water [11]. Similar correlations were obtained when the NaI was replaced by NaCl [11], or by polar non-electrolyte such as urea [11], or DMF [23]. The effect of the properties of substance X (NaI, NaCl, urea, DMF) in these correlations manifests itself in a different slope of the correlating lines. The analogous dependencies have not been observed in the non-aqueous solvents investigated thus far such as DMF or methanol. The observed correlation of the h_{XY} and $C_p(\text{int})$ indicates that in aqueous solutions, for the series of pairs consisting of the same substance X (e.g. NaI) and different non-electrolytes Y, the effect of dehydration of the molecule Y is more important than the direct interaction between X and Y when they approach each other. This former effect makes a leading contribution to the observed variation of the h_{XY} values within the series of linearly correlated pairs of substances. Other possible contributions do not influence decisively the h_{XY} variation; they remain constant or change proportionally to $C_p(\text{int})$. Therefore, a set of the h_{XY} coefficients for such selected X–Y pairs in water can serve as a thermochemical criterion, or a thermochemical relative measure of hydrophobic properties of the compound Y. (The substance X plays a role of a thermochemical probe in these pairs.) This correlation makes also possible to arrange the organic substances according to their growing hydrophobicity understood as a resultant of the hydrophobic and hydrophilic properties of their molecules. Another interesting linear correlation has been found between enthalpic pair interaction coefficients h_{XX} for homogenous pairs of natural amino acids molecules in water and “averaged” hydrophobicity parameters $P_{(\text{hydr-pho})}$ of the amino acids or their side chains [24]. It was concluded from this correlation that the mentioned interaction coefficients of L-α-amino acids in water make it possible to systematize amino acids side chains according to their affinity towards water or their hydrophobic-hydrophilic properties. Thus, appropriate h_{XX} coefficients may play the role of the parameter describing the hydrophobicity of amino acid side chains [24]. However, the enthalpic pair interaction coefficients cannot be used as a measure of hydrophobic properties of the substances when some specific interactions or chemical reactions occur in the investigated system. In that case, strong effects of the specific interactions among molecules of the both solutes give a significant impact to their values which can even dominate over the hydration effects. Then the deviations of the h_{XY} values from linear relation are observed [11].

Another method of analysis of the hydrophobic properties of dissolved substance is based on the “cage model” of hydrophobic hydration proposed by Mastroianni, Pikal and Lindenbaum [25] and developed by Somsen and his group [26,27]. According to the “cage model” the enthalpies of solution of hydrophobic compounds in water–organic solvent mixtures can be described by the equation:

$$\Delta_{\text{sol}}H^\circ(\text{M}) = (1 - x_\text{w})\Delta_{\text{sol}}H^\circ(\text{S}) + x_\text{w}\Delta_{\text{sol}}H^\circ(\text{W}) + (x_\text{w}^n - x_\text{w})Hb(\text{W}) \quad (3)$$

in which $\Delta_{\text{sol}}H^\circ(\text{M})$, $\Delta_{\text{sol}}H^\circ(\text{S})$ and $\Delta_{\text{sol}}H^\circ(\text{W})$ denote the enthalpies of solution in the mixture, in the cosolvent and in water, respectively, $Hb(\text{W})$ is the enthalpic contribution of hydrophobic hydration in water and n is the number of water molecules hydrating one alkyl group. The expression: $(x_\text{w}^n - x_\text{w})\cdot Hb(\text{W})$ describes deviations from the additivity of the dissolution enthalpy in the mixed solvent caused by hydrophobic hydration of hydrophobic solute (Eq. (4)).

$$(x_\text{w}^n - x_\text{w})Hb(\text{W}) = \Delta_{\text{sol}}H^\circ(\text{M}) - [(1 - x_\text{w})\Delta_{\text{sol}}H^\circ(\text{S}) + x_\text{w}\Delta_{\text{sol}}H^\circ(\text{W})] \quad (4)$$

The assumptions of the model are fulfilled in the mixtures of water with DMSO and DMF [26].

The “cage model” was applied in our laboratory for the investigations of the hydrophobic properties of crown-ethers, when we studied the thermodynamic functions of crown-ether−cation complex formation and the complex hydration in aqueous solvent mixtures [28,29]. The dissolution enthalpies of 12-C-4, 15-C-5, 18-C-6 and B-15-C-5 in the mixtures of water with DMSO and with DMF could be very well fitted to the model equation [30,31]. Determined by the least square analysis the hydrophobic hydration parameters for the examined crown-ethers in the both mixed solvents were practically the same. The $Hb(\text{W})$ values become more exothermic when the number of CH_2 groups in the crown-ether molecule grows, as it could be expected. A contribution from each CH_2 group in the total $Hb(\text{W})$ enthalpy amounts to 4,7 ± 0,3 kJ which is a very close value to the analogous one determined by Heuvelsland et al. in the case of hydrophobic hydration of amines [27].

The results of examination of hydrophobic properties of different substances performed by means of the “cage model” appeared to be consistent with the results obtained from the analysis of the enthalpic pair interaction coefficients. The $Hb(\text{W})$ parameters determined for large number of non-electrolytes (alcohols, amides, amines) are linearly correlated with the h_{XY} values for DMF−non-electrolyte pairs in water for the same non-electrolytes [7].

Our studies on thermochemical properties of crown-ether solutions contained also solutions in the mixtures of water with other organic cosolvent, namely: DMA, HMPA, FA, NMF, PrOH and AN [28–31]. These mixtures do not satisfy the assumptions of the "cage model" due to the different reasons, for instance: hydrophobic properties of HMPA and PrOH, or ability to form hydrogen-bonded structure in the case of FA, NMF and PrOH. The shape of the dissolution enthalpy curves in these mixtures differs from that for the mixtures of water with DMF or DMSO. It can be expected that the thermal effect of the dissolution in these mixed solvents includes contributions not only from hydrophobic hydration of the solute and from gradual change of the solute solvation shell composition. It should contain some contributions from possible specific interaction of the crown-ether molecule with the cosolvent molecules (preferential solvation or complex formation) and competition because of hydration of cosolvent molecules. For this reason, the equation describing deviations from additivity of the crown-ether dissolution enthalpy in these mixtures (Eq. (4)) should contain additional energetic effect, (ΔH^*), which illustrate the interactions in solution, other than hydrophobic hydration of the solute. The "corrected" equation has a form [30,31]:

$$\Delta H^{\mathrm{E}} = \Delta_{\mathrm{sol}}H^\circ(\mathrm{M}) - [(1-x_{\mathrm{w}})\Delta_{\mathrm{sol}}H^\circ(\mathrm{S}) + x_{\mathrm{w}}\Delta_{\mathrm{sol}}H^\circ(\mathrm{W})] = (x_{\mathrm{w}}^n - x_{\mathrm{w}})Hb(\mathrm{W}) + \Delta H^* \tag{5}$$

or, more convenient one:

$$\Delta H^* = \Delta_{\mathrm{sol}}H^\circ(\mathrm{M}) - [(1-x_{\mathrm{w}})\Delta_{\mathrm{sol}}H^\circ(\mathrm{S}) + x_{\mathrm{w}}\Delta_{\mathrm{sol}}H^\circ(\mathrm{W})] - (x_{\mathrm{w}}^n - x_{\mathrm{w}})Hb(\mathrm{W}) \tag{6}$$

It can be expected that strong interactions between water and the cosolvent will result in endothermic shift of the ΔH^* function, while negative, exothermic shift reflects a preferential solvation in solution.

The ΔH^* values for 15-C-5 solutions in the mixtures of water with HMPA, DMA, PrOH, FA, NMF, and AN were calculated from the appropriate dissolution enthalpy data using the $Hb(\mathrm{W})$ and n values for the solute determined on the base of application of the cage model to solutions in water–DMF mixtures [30,31]. The ΔH^* function in the mixtures of water with HMPA and DMA for 15-C-5 exhibits positive values in the range of high water content, and the values close to zero when the water content decreases [30]. This endothermic shift of the analyzed function ΔH^* is connected with the hydrophobic hydration of the organic cosolvent. The molecules of the crown-ether interact first of all with those water molecules which are not directly associated with the hydrophobic cosolvent molecules. In order to complete the solvation shell of the crown-ether molecule in these mixtures some energy loss is necessary to release appropriate number of water molecules. The observed endothermic effect is much higher in the mixtures containing HMPA that is known as one of the most hydrophobic solvents [30]. The ΔH^* function in mixtures of water with FA and NMF has negative values within the whole range of the mixed solvent composition [30]. As it was suggested earlier, such behavior can be connected with the preferential solvation (PS) of the crown-ether in the mixed solvent. For a quantitative description of the enthalpic effect of PS it is possible to use the simplest version of the thermodynamic theory on PS of Covington et al. [32,33] and developed by Balk and Somsen [34]. The theory analyzes the change in composition of the solvation shell with solvent composition for a given solute S in a mixture M of solvent components W and P. When the mixture becomes richer in one of its components, the change in the composition of the solvation shell of S is described by a successive series of "r "equilibriums, where r is the solvation number:

$$\mathrm{S}(\mathrm{W}_{i-1}\mathrm{P}_{r+1-i}) + \mathrm{W} \rightleftarrows \mathrm{S}(\mathrm{W}_i\mathrm{P}_{r-i}) + \mathrm{P}(1 \le i \le r) \tag{7}$$

The final equation for the excess enthalpic effect of PS has a form:

$$\Delta H_{\mathrm{PS}}^{\mathrm{E}}(\mathrm{M}) = rRT\left[\frac{(1-x_{\mathrm{w}})}{(1-x_{\mathrm{w}}) + K^{1/r}x_{\mathrm{w}}} - (1-x_{\mathrm{w}})\right]\ln K^{1/r} \tag{8}$$

This function is negative over the whole mole fraction region ($K^{1/r} > 0$), thus resulting in an exothermic contribution to the enthalpy of solution [34].

In the case of water–FA and water–NMF mixtures, the model reproduces the ΔH^* curves within the experimental error, $\Delta H^* \cong \Delta H_{\mathrm{PS}}^{\mathrm{E}}(\mathrm{M})$. The parameter $K^{1/r}$ is smaller than one, which means that the functional groups are preferentially solvated by the organic cosolvent [30].

The most complex shape of the ΔH^* curve is observed for solutions of the crown-ethers in water–PrOH and water–AN mixtures [31]. The examined function goes through a maximum in the range of high water content, similarly as in the systems containing HMPA or DMA, but it exhibits high negative values when water content in the mixture decreases. One may suppose that within the composition range where the values of ΔH^* are negative, the preferential solvation of the crown-ether molecules in the mixed solvent occurs. In a mixture of water with PrOH, hydrogen bonds may be formed between crown-ether molecules and PrOH. In a mixture of water with AN, a complex of the crown-ether molecule with AN probably is formed, similarly as was found in the case of 18-C-6 + AN. On the other hand, in the water-rich area, the endothermic effect results probably from strong interactions between water and the cosolvent. The observed effect seems to be then associated with the structure and properties of the mixed aqueous–organic solvent. This conclusion is confirmed by the similarity of the shape of the obtained functions $\Delta H^*(\mathrm{M}) = f(x_{\mathrm{w}})$ to the shape of the mixing enthalpy of water with AN and PrOH curves, $\Delta H^{\mathrm{E}} = f(x_{\mathrm{w}})$. Moreover, the both discussed functions exhibit characteristic minima and maxima at similar compositions of the mixed solvent [31].

The mentioned above model of preferential solvation was also successfully applied to description of the NaI dissolution enthalpy in several organic solvent mixtures, among others in the mixtures of acetonitrile with methanol [35]. It fits well also the single ion (Na^+) transfer enthalpies in these mixtures [36].

Naturally, there are yet known other models applicable for analysis of the dissolution enthalpy data. Some of them were also used in our laboratory; however their discussion is beyond the scope of this presentation.

3. Heat capacity

The aqueous solutions of surfactants and some alkoxyethanols (e.g. butoxyethanol, BE) show many anomalous physical properties which are attributed to the formation of molecular and micellar aggregates in aqueous solutions. Among others heat capacity of these solutions exhibits a maximum at the critical micelle concentration *cmc*. Numerous papers have been devoted to examination of the micelles formation phenomena. Analysis of the heat capacity as a function of concentration of the solution is one of the important methods used in these studies. Recently, we have 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 [37]. The details of the two-point scaling concept were presented by Wojtczak in his paper published earlier [38]. This model was successfully used for description of the temperature dependence of several basic thermodynamic functions for solid substances, within the temperature range where phase transition phenomena occur [38].

In order to describe structural changes occurring in solution, the model has been reformulated for the case when the thermodynamic functions depend on the other variable: molal concentration expressed by solution molality m. In this reformulation, we considered a mixture which can appear in two phases confined by the stability points of the molality m_{sp} and m_{sf} which refer to the phase of homogeneous structure, denoted as $s = 1$, and the phase of micellar structure denoted as $s = 2$. The values m_{sp} are the stability points for lower limits of the concentration of phase s, while the values m_{sf} mean the stability points for upper limits of the concentration of phase s. The singularities of the thermodynamic potential function are related to the stability points: m_{sp} and m_{sf} which determine the region of phase coexistence [37].

The function predicted by the two-point scaling approach describing the partial molal heat capacity $C_{p,2}(m)$ in the phase $s = 1$, for $m \leq m_f$ can be written in the form:

$$C^{f}_{p,2} = C^{0,f}_{p,2}\left(1 - \frac{m}{m_f}\right)^{-\alpha_1} \tag{9}$$

The same for the phase $s = 2$, where $m \geq m_p$ can be written:

$$C^{p}_{p,2} = C^{0,p}_{p,2}\left(\frac{m}{m_p} - 1\right)^{-\alpha_2} \tag{10}$$

In these formulas α_1 and α_2 stand for the critical exponents while $C^{0,f}_{p,2} = C^{f}_{p,2}$ $(m = 0)$ and $C^{0,p}_{p,2} = C^{p}_{p,2}$ $(m = 2m_p)$ are the constants to be determined in the fitting procedure. The critical molalities m_C which correspond to the *cmc* values are determined as the crossing points of the $C^{f}_{p,2}$ and the $C^{p}_{p,2}$ functions. The expressions describing another function illustrating the considered phenomena, the apparent molar heat capacity C_ϕ were also derived from this model.

The two-point scaling model was applied for the firs time to analysis of the $C_{p,2}(m)$ function for 2-butoxyethanol (BE) solutions in water within a wide temperature range [37]. The experimental data were very well fitted to the model equations. The determined range of the phase coexistence region $\langle m_p, m_f\rangle$ becomes wider as the temperature increases, what seems to be reasonable. The values of critical exponents $\alpha_1 = 0.125$, $\alpha_2 = 0.33$ remain constant within the whole examined range of the temperature. Moreover, it was shown that in the light of the discussed model the phase separation line has its internal structure, namely the critical molality has two different origins in the region of higher and lower temperatures. It is noteworthy, that the two curves predicted by two-point model fit better the points corresponding to higher temperatures than the best fitting taken by means of one curve that approaches these points.

The two-point scaling approach was used also for analysis of C_p data for simple micellar system decyltrimethylammonium bromide (C_{10}TAB) in water [39] and for the pseudo-ternary system water/dodecyltrimethylammonium bromide/hexan-1-ol [40]. In the latter system, hexan-1-ol plays role of the co-surfactant; the molar ratio of the surfactant to co-surfactant was 1:1, and for all the calculations the both surfactants were treated as one compound. It appeared that also in these cases the $C_{p,2}$ and C_ϕ data were very well described by the model [39,40].

The most interesting observation is that in both mentioned above systems the critical exponent α_1 takes a value 0.125 and remains constant within the whole examined temperature range as it was observed in the case of 2-butoxyethanol–water mixtures. The value $\alpha_1 = 0.125$ seems to be characteristic for the regular solutions region of these systems. The parameter α_2 values depend on the kind of solute and temperature. As the critical coefficients are connected with the order parameters [38] we expect that it might be possible to find a correlation between their values and the structure of the examined phase.

The presented two-point scaling approach seems to be very useful for the analysis of C_p function for microheterogenous and micellar systems. It confirms the existence an interval of molalities around the critical molality where a variety of structural forms can appear. The phase transition is not of the sharp jump nature but the isotropic structures co-exist in some interval of concentrations and, above the upper limit for the stability concentration, they pass into micellar lower dimensionality structures.

The presented results demonstrate clearly, that the solution calorimetry data, when used in appropriate way can supply large information about molecular interactions in solution. And even now, when non-calorimetric methods of investigations seem to dominate in experimental sciences, calorimetry is still a significant tool in solution chemistry.

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