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THERMODYNAMICS OF SODIUM DICLOFENAC SALT AQUEOUS SOLUTIONS AT VARIOUS TEMPERATURES

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Enthalpies of solution and dilution of aqueous solutions of sodium diclofenac salt were measured by isoperibolic calorimeter at 293.15, 298.15, 303.15, 308.15 and 318.15 K. The concentration of the electrolyte was restricted to solubility salt at various temperatures and did not exceed 0.035–0.057 mol kg^{-1} values depending on the studied temperature. The virial coefficients were derived from Pitzer's model and the excess thermodynamic functions of both the solution and the components of the solution were calculated. The analysis of thermodynamic characteristics of the solution from concentration and temperatures was carried out and discussed.

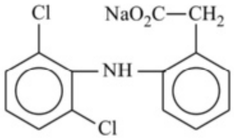
Keywords: *calorimetry, dilution, isoperibolic calorimeter, Pitzer model, sodium diclofenac salt, solution, thermodynamic functions*

Introduction

One of the key issues in drug design is to let the molecules actually reach their target. Each stage of the processes involved, as there are liberation (dissolution), absorption, distribution, and passive transport, is determined by the solvation characteristics of the drug molecules. So far, these questions have been addressed mainly from the point of view of relative thermodynamic functions in the form of partitioning and distribution coefficients (log*P*, log*D*). In our previous work [1–3] we have approached this problem by analysis of the thermodynamic functions in absolute energetic scales, in order to understand the mechanisms and driving forces of the drug transport and drug delivery processes.

Solution (dilution) enthalpy is an important thermodynamic function and may be used effectively for characterization of different properties of drug molecules [4, 5]. For example, solution enthalpies have been applied to describe crystallinity of drug amorphous materials [6] and to analyze various energetic drug-solvents interactions terms [7, 8]. There are some studies devoted to studying heat effects of nucleation process to obtain information about the stability of pharmaceutical solutions [9]. Moreover, in literature there is a semi-empirical approach proposed by Pitzer [10, 11] describing long- and short-distance interionic interactions of salts in solutions. This approach gives opportunity to consider the thermochemical data within framework of the model for both concentration and temperature intervals and to calculate the whole sets of the excess solution thermodynamic functions based on thermochemical experiments only.

As a subject for the present investigation it has been chosen sodium diclofenac (Scheme 1) because the compound is a wide used non-steroidal anti-inflammatory drug and in the literature it has been described the various properties [7, 12]. However, solvation characteristics of the substance have not studied yet and this fact is a barrier to carry out analysis between the outlined properties at one side, and pharmacodynamic and pharmacokinetic data – at other. Therefore, the aim of our investigations was thermochemical study of sodium diclofenac aqueous solutions at wide concentration and temperature intervals (important for pharmaceutical and medical reasons) and thermodynamic characterization of this system by Pitzer's approach.



Scheme 1

Experimental

Materials

Sodium diclofenac salt (Benzeneacetic acid, 2-[(2,6-dichlorophenyl)amino]-, monosodium salt; Na_DC, pharmaceutical grade) was a gift from FARCHEMIA, Bergamo, Italy. Before the thermochemical experi-

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ments the salt was re-crystallized from water and then dried in the oven at 383 K for 8 h. The DSC curves did not display any heat events corresponding crystallohydrates in the temperature interval from 298 up to the temperature decomposition of the compound (higher than 573 K). Before the calorimetric experiments the compound was kept in a water-protected desiccator.

Methods

DSC experiments

Thermal analysis using a DSC method was carried out employing an automatic thermal analyzer system (Mettler 821^e). The data processing system (Mettler 821^e/500/847 thermo-cryostat) was connected to the thermal analyzer. Sealed and holed aluminum pans were used for all the samples. Temperature calibrations were made using indium as the standard. An empty pan, sealed in the same way as the sample, was used as a reference. The thermograms were run at a scanning of 10 K min^{-1}, from 298 to 573 K.

Solution calorimetry

Enthalpies of solution and dilution were measured using an isoperibolic calorimeter of ampoule type with volume of the vessels 30 and 50 cm^3 [13, 14]. The temperature stability was better than $2\cdot10^{-3}$ K. The accuracy of mass measurements corresponded to $\pm10^{-6}$ g. The calorimeter was calibrated using KCl (analysis, grade >99.5%, from Merck) in water in a wide concentration interval with a number of measurements of more than 10. The obtained standard value of solution enthalpy was 17225±50 J mol^{-1}. This is in good agreement with the value 17217±33 J mol^{-1} recommended by the IUPAC [15].

Calculation procedure

Everything calculations have been carried out on base of experimental data of the solution enthalpy Na_DC in water ($\Delta_{\text{sol}}H^{\text{m}}$) and the molar dilution enthalpy ($\Delta_{\text{dil}}H^{\text{m}_\text{i}\to\text{m}_\text{f}}$) of the concentrated solution from the initial (m_i) to final (m_f) concentrations:

$$\Delta_{\text{sol}}H^{\text{m}_\text{i}}=\Delta_{\text{sol}}H^{\text{m}_\text{f}}-\Delta_{\text{dil}}H^{\text{m}_\text{i}\to\text{m}_\text{f}}=\Delta_{\text{sol}}H^{\text{m}_\text{f}}-L_\Phi \quad (1)$$

where L_Φ is a relative partial molar enthalpy of the solution electrolyte (Na_DC) at molality of m.

At the other hand, the L_Φ-value can be described from the Pitzer's model [16] as:

$$\begin{aligned}L_\Phi=&|z_\text{M}z_\text{X}|(2A_\text{H}/3b)\ln(1+bI^{1/2})-\\&-2\nu_\text{M}\nu_\text{X}RT^2(mB'_{\text{MX}}+m^2C'_{\text{MX}})\end{aligned}\quad (2)$$

where

$$\begin{aligned}B'_{\text{MX}}=&(\partial\beta^{(0)}_{\text{MX}}/\partial T)_{\text{I,P}}+\\&+(2/\alpha^2I)(\partial\beta^{(1)}_{\text{MX}}/\partial T)_{\text{I,P}}[1-(1+\alpha I^{1/2})\exp(-\alpha I^{1/2})]\end{aligned}\quad (3)$$

$$C'_{\text{MX}}=0.5(v_\text{M}v_\text{X})^{1/2}(\partial C^\Phi_{\text{MX}}/\partial T)_{\text{I,P}} \quad (4)$$

where I is the ionic strength; z_M and z_X are the charges of cation and anion, respectively; ν_M and ν_X are number of cations and anions in the electrolyte molecule (Na_DC); A_H is the theoretical slope for the enthalpy (limit of Debye–Hückel slope) and is borrowed from [17] (Table 1). The first term of the Eq. (2) corresponds to long-distance electrostatic interactions. The second term corresponds to short-distance interactions and includes the various virial coefficients $\beta^{(0)}_{\text{MX}}$, $\beta^{(1)}_{\text{MX}}$ and C^Φ_{MX}. The b and α-values were chosen as 1.2 and 2.0 kg$^{1/2}$ mol$^{1/2}$, respectively, as recommended by [10, 18]. The temperature dependencies of the virial coefficients have been interpolated by equations presented in the next section (Tables 3 and 4) using model described in [18].

The equations describing the excess solution thermodynamic functions can be presented as [17–19]:

$$H^\text{E}\equiv L_\Phi=-\Delta_{\text{dil}}H^{\text{m}\to0} \quad (5)$$

$$\overline{L_1}=-0.5m^{3/2}M_1(\partial L_\Phi/\partial m^{1/2}) \quad (6)$$

$$\overline{L_2}=L_\Phi+0.5m^{1/2}(\partial L_\Phi/\partial m^{1/2}) \quad (7)$$

$$\begin{aligned}&\Phi(T_2)-\Phi(T_1)=\\&=(m^{1/2}/2\nu R)\int_{\text{T}_1}^{\text{T}_2}[\partial L_\Phi/\partial m^{1/2})\text{d}(1/T)\end{aligned}\quad (8)$$

$$\begin{aligned}&\ln[\gamma(T_2)/\gamma(T_1)]=\\&=(1/\nu R)\int_{\text{T}_1}^{\text{T}_2}[L_\Phi+(m^{1/2}/2)(\partial L_\Phi/\partial m^{1/2})d(1/T)]\end{aligned}\quad (9)$$

$$C^\text{E}_\text{P}=\overline{C}_\text{P}-C^0_\text{P}=(\partial L_\Phi/\partial T)_\text{P} \quad (10)$$

where Φ and γ are osmotic and activity coefficients, respectively; $\overline{L_1}$ and $\overline{L_2}$ are the partial molar enthalpies of solvent and solute of the studied solution; ν is a number of ions of Na_DC (ν=2); M_1 is the molar mass of water; C^E_P is the excess heat capacity of solution at constant pressure.

Results and discussion

The experimental data of the solution and dilution enthalpies of Na_DC in water at the various concentrations and temperatures are presented in Tables 1, 2 and in Fig. 1 as well.

As it can be seen from Fig. 1, the endothermic effect increases at increasing of both the concentration of the salt up to 0.01 mol kg^{-1} and the temperature. It

Table 1 Solution enthalpies, $\Delta_{sol}H^m$ (kJ mol^{-1}), of Na_DC in water at various temperatures[a]

m/mol kg^{-1}	$\Delta_{sol}H^m$	*m*/mol kg^{-1}	$\Delta_{sol}H^m$	*m*/mol kg^{-1}	$\Delta_{sol}H^m$	*m*/mol kg^{-1}	$\Delta_{sol}H^m$
T=293.15 K, A_H=1315 J kg$^{1/2}$ mol$^{-3/2}$							
0.00045	–3.135[b]	0.00098	–3.270[b]	0.00479	–2.031	0.01316	–0.155
0.00077	–4.327	0.00118	–3.633	0.00616	–1.475	0.01615	0.225
0.00078	–4.266[b]	0.00201	–2.804[b]	0.00876	–1.692	0.01938	0.353
0.00083	–3.578[b]	0.00218	–3.084[b]	0.00914	–0.635	0.02895	0.345
0.00090	–2.740[b]	0.00349	–2.524	0.01314	–0.176	0.03505	0.900
0.00094	–4.133	0.00387	–2.079				
T=298.15 K, A_H=1448 J kg$^{1/2}$ mol$^{-3/2}$							
0.00066	1.320[b]	0.00592	2.260	0.01608	3.751	0.02871	4.486
0.00439	2.068	0.00891	3.017	0.02081	4.450	0.03314	4.774
0.00499	2.159	0.01305	3.648	0.02174	4.427	0.04412	5.091
T=303.15 K, A_H=1590 J kg$^{1/2}$ mol$^{-3/2}$							
0.00051	1.582[b]	0.00170	2.571	0.01425	3.907	0.03505	4.568[b]
0.00057	1.626[b]	0.00212	2.680[b]	0.02008	4.202	0.04301	4.033[b]
0.00104	1.779	0.00224	1.991	0.02389	3.857	0.04744	2.318
0.00128	2.069[b]	0.00789	2.802	0.02895	4.106[b]		
T=308.15 K, A_H=1740 J kg$^{1/2}$ mol$^{-3/2}$							
0.00062	3.453	0.00104	3.621[b]	0.00437	4.674	0.01128	6.079
0.00066	3.822[b]	0.00149	4.046	0.00552	5.332	0.02519	6.439
0.00071	3.964[b]	0.00209	3.436[b]	0.00979	5.746	0.03444	6.488
						0.04580	5.909
T=318.15 K, A_H=2069 J kg$^{1/2}$ mol$^{-3/2}$							
0.00105	5.689[b]	0.00232	6.429[b]	0.00435	6.607	0.01963	9.269
0.00119	6.627[b]	0.00268	6.329	0.00543	7.412	0.02576	9.103
0.00131	5.180	0.00293	6.695[b]	0.00631	6.783[b]	0.02984	8.839
0.00142	6.577[b]	0.00301	6.995[b]	0.00961	8.221	0.04410	9.224
0.00191	6.515[b]	0.00373	6.710[b]	0.01036	8.627	0.05698	8.985

[a] *m* – molality (mol kg^{-1}) of the solutions obtained by dissolution of the salt; [b] $\Delta_{sol}H^m$ obtained by recalculation data from the dilution experiments

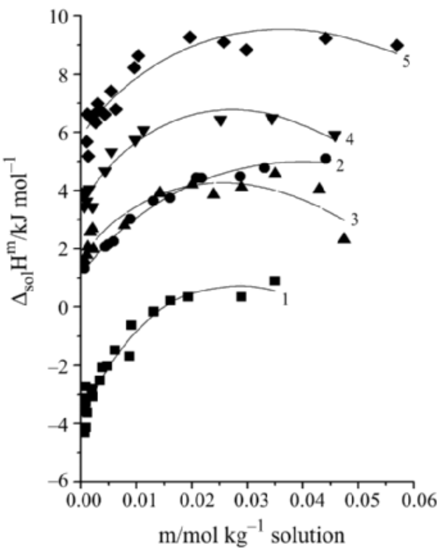

Fig. 1 Concentration dependencies of Na_DC solution enthalpies in water at the different temperatures: 1 – 293.15, 2 – 298.15, 3 – 303.15, 4 – 308.15 and 5 – 318.15 K

should be mentioned, that the function of the heat effects from concentration is practically independent from the concentration at the values higher than 0.01 mol kg^{-1}. It is interesting to note, that the Na_DC solvation enthalpy is decreased with temperature increasing. It may be assumed, that the solvation process of the studied ionic mixture is determined by the cavernous mechanism. At the temperature increasing the primary water structure is destroyed and becomes more close–packing structure: as a consequence, the endothermic cost to create appropriate cavity volume in the solvent to be situated for the solute molecules arises.

In order to estimate the excess thermodynamic functions the temperature independent q_i parameters were calculated. The results are summarized in Tables 3 and 4.

Dependencies of the relative characteristics of the activity and osmotic coefficients on concentration are presented in Fig. 2. It should be noted that the outlined functions are not linear. Moreover, the function $\Phi_T–\Phi_{293.15}=f(m)$ has the inversion point at 0.027 *m*. The minimal value of the activity coefficient corresponds to 0.02 *m*, whereas for the osmotic coefficient it corresponds to 0.012 *m*.

Dependencies of the excess solution heat capacities (C_p^E) at various concentrations are shown in Fig. 3. It is not difficult to see that these functions per-

Table 2 Dilution enthalpies, $-\Delta_{dil}H^{m_i \rightarrow m_f}$ (kJ mol^{-1}), of Na_DC in water at various temperatures

m_i/mol kg^{-1}	m_f/mol kg^{-1}	$-\Delta_{dil}H^{m_i \rightarrow m_f}$
	T=293.15 K	
0.01316	0.00045	2.980
0.02895	0.00218	3.429
0.02895	0.00098	3.615
0.02895	0.00201	3.149
0.02895	0.00083	3.923
0.03505	0.00078	5.166
0.03505	0.00090	3.640
	T=298.15 K	
0.01328	0.00066	2.328
	T=303.15 K	
0.02895	0.00097	2.327
0.03505	0.00051	2.986
0.03505	0.00057	2.942
0.03505	0.00162	1.997
0.04301	0.00099	2.254
0.04301	0.00212	1.353
0.04301	0.00128	1.964
	T=308.15 K	
0.02519	0.00066	2.617
0.02519	0.00071	2.475
0.04580	0.00104	2.288
0.04580	0.00209	2.473
	T=318.15 K	
0.03505	0.00091	4.935
0.04301	0.00142	2.647
0.04301	0.00301	2.229
0.05698	0.00105	3.296
0.05698	0.00232	2.556
0.05698	0.00119	2.358
0.05698	0.00293	2.290
0.05698	0.00191	2.470
0.05698	0.00373	2.275
0.05698	0.00631	2.202

form a linear trend from temperature with inversion intervals around 305.15–310.15 K. This regularity testifies that temperature factor has an essential influence on the structure of the studied solution. Moreover, while the concentration of the solution increases, the C_p^E-function is more sensitive to the temperature variation.

In order to analyze the solution behavior in detail the relative partial molar enthalpies for the both water ($\overline{L_1}$) and Na_DC ($\overline{L_2}$) were considered [17]. Let us first consider thermodynamic properties of the water molecules in the solution. The results of calculations of $\overline{L_1}=f(m)$ function at the various temperatures are collected in Fig. 4. It should be mentioned that at the low Na_DC concentration the structure of the water molecules of the solution rebuilds essentially: $\overline{L_1}$-values are changed from –1000 up to 4000 J mol^{-1}. The $\overline{L_1}=f(m)$ function has a minimum at the concentration around 0.015–0.025 mol kg^{-1} (depending on T). The minimum is shifted to the region of the lower Na_DC concentrations at 293.15–313.15 K, whereas at 303.15–313.15 K the minimum is shifted to the interval with higher Na_DC concentrations. At m<0.03 mol kg^{-1}, Na_DC molecules promote an increase of interactions between the water molecules in the solution (structuring effect): negative $\overline{L_1}$-values (Fig. 4a). An increase of the Na_DC concentration leads to decreasing interactions between the solvent molecules in the solution (disordering effect): positive $\overline{L_1}$-values (Fig. 4a).

For the next step, let us analyze what is the behavior of the solute molecules in the solution. The $\overline{L_2}=f(T)$ and $\overline{L_2}=f(m)$ dependencies are mirror images of $\overline{L_1}$, therefore the Figures are not presented here.

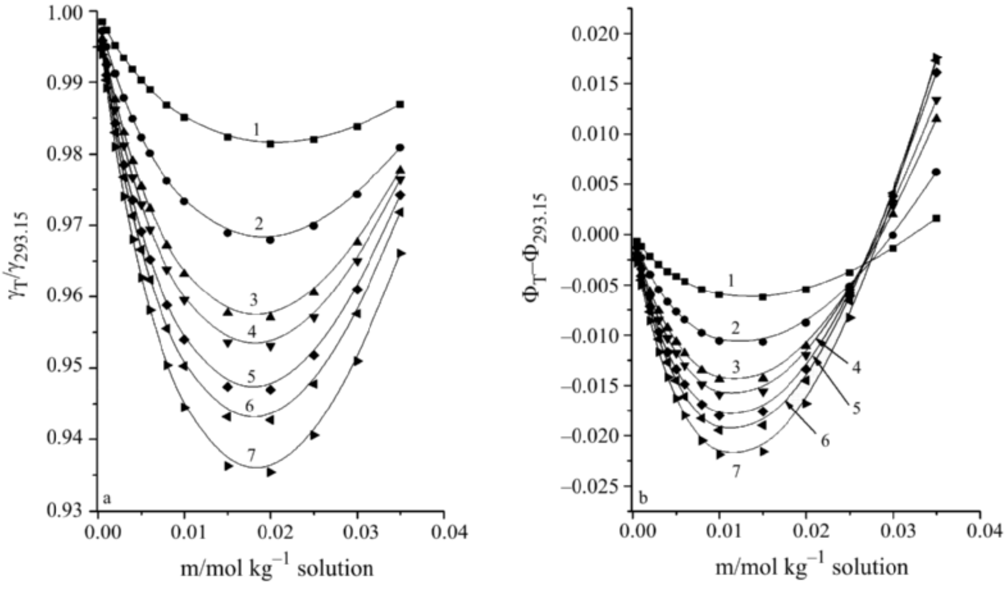

Fig. 2 Dependencies of a – $\gamma_T/\gamma_{293.15}$ and b – (Φ_T–$\Phi_{293.15}$) *vs*. Na_DC concentration at various temperatures: 1 – 298.15, 2 – 303.15, 3 – 308.15, 4 – 310.15, 5 – 313.15, 6 – 315.15 and 7 – 318.15 K

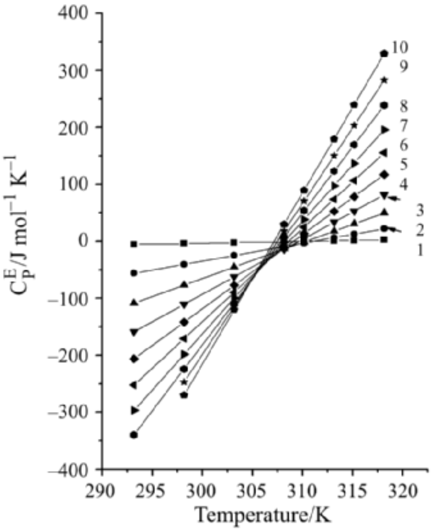

Fig. 3 Dependencies of C_p^E *vs.* temperature at various concentrations: 1 – 0.0005, 2 – 0.005, 3 – 0.01, 4 – 0.015, 5 – 0.02, 6 – 0.025, 7 – 0.03, 8 – 0.035, 9 – 0.04 and 10 – 0.045 mol kg^{-1}

The maximum of $\overline{L_2}=f(m)$ function corresponds to concentration interval 0.015–0.025 mol kg^{-1}. The region with $m<0.02$ mol kg^{-1} describes the weak hydration of Na_DC molecules with water, whereas at $m>0.02$ mol kg^{-1} hydration increases, probably due to both the destruction of the primary water structure and the association of solute molecule processes.

The differential characteristics of the components of the solution ($\overline{L_1}$ and $\overline{L_2}$) are connected with the partial molar heat capacities by the following equations [17]:

Table 3 Temperature independent parameters q_i for calculation of L_Φ-values of Na_DC

Parameters[a]	Values
q_2	$(2.26\pm0.24)\cdot10^6$
q_3	$(1.59\pm0.16)\cdot10^4$
q_4	–27.2±2.9
q_9	–5.9±1.6
q_{10}	$(8.4\pm2.5)\cdot10^{-3}$
$s(L_\Phi)$	444

[a] $\beta_{MX}^{(0)}=q_1+q_2[(T_R-T)/TT_R]+q_3\ln(T/T_R)+$
$+q_4(T-T_R)+q_5(T^2-T_R^2)$;
$\beta_{MX}^{(1)}=q_6+q_9(T-T_R)+q_{10}(T^2-T_R^2)$;
$C_{MX}^{\Phi}=q_{11}+q_{12}[(T_R-T)/TT_R]+q_{13}\ln(T/T_R)+q_{14}(T-T_R)$
where T_R=298 K

Table 4 The $(\partial\beta_{MX}^{(0)}/\partial T)_{I,P}$[a] and $(\partial\beta_{MX}^{(1)}/\partial T)_{I,P}$[b] values to calculate L_Φ-values of Na_DC in water at various temperatures[c]

T/K	$(\partial\beta_{MX}^{(0)}/\partial T)_{I,P}$/ kg mol^{-1} K^{-1}	$-(\partial\beta_{MX}^{(1)}/\partial T)_{I,P}$/ kg mol^{-1} K^{-1}	$s(L_\Phi)$/J mol^{-1}
293.15	0.692±0.124	1.005±0.078	476
298.15	0.657±0.125	0.921±0.052	409
303.15	0.610±0.127	0.837±0.027	480
308.15	0.550±0.130	0.7530±0.0017	446
310.15	0.524±0.132	0.7194±0.0085	–
313.15	0.481±0.134	0.669±0.024	–
315.15	0.450±0.137	0.635±0.034	–
318.15	0.402±0.140	0.585±0.049	437

[a] $(\partial\beta_{MX}^{(0)}/\partial T)_{I,P}=-q_2/T^2+q_3/T+q_4+2q_5T$;
[b] $(\partial\beta_{MX}^{(1)}/\partial T)_{I,P}=q_9+2q_{10}T$;
[c] $(\partial C_{MX}^{\Phi}/\partial T)_{I,P}=-q_{12}/T^2+q_{13}/T+q_{14}=0$ within the studied temperature interval

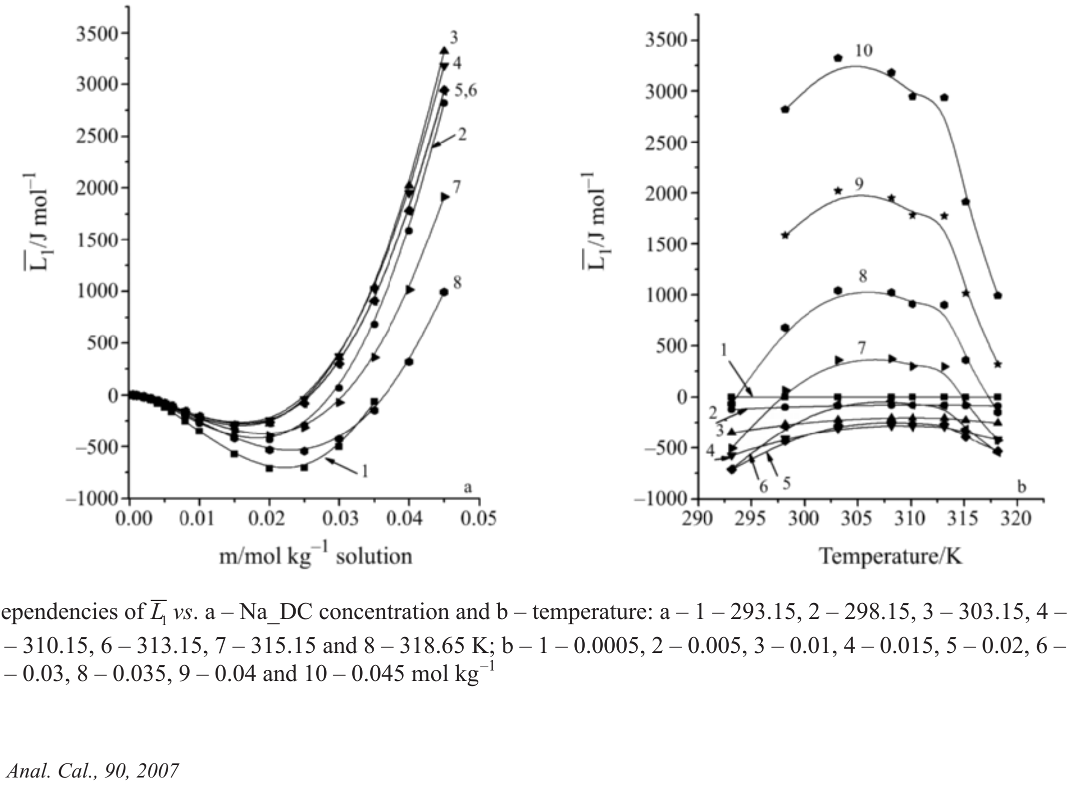

Fig. 4 Dependencies of $\overline{L_1}$ *vs.* a – Na_DC concentration and b – temperature: a – 1 – 293.15, 2 – 298.15, 3 – 303.15, 4 – 308.15, 5 – 310.15, 6 – 313.15, 7 – 315.15 and 8 – 318.65 K; b – 1 – 0.0005, 2 – 0.005, 3 – 0.01, 4 – 0.015, 5 – 0.02, 6 – 0.025, 7 – 0.03, 8 – 0.035, 9 – 0.04 and 10 – 0.045 mol kg^{-1}

$$\partial\overline{L_1}/\partial T=\overline{C}_{p1}-\overline{C}^{\,0}_{p1} \qquad (11)$$

$$\partial\overline{L_2}/\partial T=\overline{C}_{p2}-\overline{C}^{\,0}_{p2}=\overline{C}_{p2}-\Phi^{\,0}_{C_p} \qquad (12)$$

where $\overline{C}_{p1}$ and $\overline{C}_{p2}$ are the partial molar heat capacity of water and Na_DC, respectively; $\overline{C}^{\,0}_{p1}$ and $\overline{C}^{\,0}_{p2}$ are the partial molar heat capacity at infinite dilution (for the water component it corresponds to the water heat capacity); $\Phi^0_{C_p}$ is the apparent molar heat capacity of Na_DC at $m=0$.

The temperature coefficients $\partial\overline{L_1}/\partial T$ and $\partial\overline{L_2}/\partial T$ (Fig. 4) have different signs: at $T<303.15$ K $\partial\overline{L_1}/\partial T>0$ and $\partial\overline{L_2}/\partial T<0$; $T>308.15$ K $\partial\overline{L_1}/\partial T<0$ and $\partial\overline{L_2}/\partial T>0$. In other words at $T<303.15$ K $\overline{C}_{p1}>\overline{C}^{\,0}_{p1}$ and $\overline{C}_{p2}<\overline{C}^{\,0}_{p2}$ (structuring effect of the water molecules in the solution), whereas at $T>308.15$ K $\overline{C}_{p1}<\overline{C}^{\,0}_{p1}$ and $\overline{C}_{p2}>\overline{C}^{\,0}_{p2}$ (disordering effect of water in the solution). It should be noted, that at the extremum point ($\overline{C}_{p1}\cong\overline{C}^{\,0}_{p1}$) the partial molar heat capacity of water molecules in the solvent is equal to the pure water heat capacity and $\overline{C}_{p2}\cong\overline{C}^{\,0}_{p2}$ corresponds to equal values of the Na_DC partial molar heat capacity in the solution and the Na_DC partial molar heat capacity at infinite dilution.

Conclusions

The complete set of the thermodynamic characteristics of Na_DC aqueous solution was investigated at the whole concentration interval and physiologically important temperature region. The particular concentration value of the studied solution where the osmotic coefficients are not dependent on temperature (inversion points) was established. The three concentration intervals of the solution under investigation where the hydration characteristics of the Na_DC molecules essentially differ from each other were defined.

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