

Dimerization of methylene blue in aqueous solutions of inorganic electrolytes

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Using the strong electrolytes theory and statistical methods, the concentration equilibrium constants for methylene blue dimerization in aqueous solutions of inorganic electrolytes were evaluated as a function of ionic strength of the solutions. Thus the values of thermodynamic equilibrium constant were obtained. The reaction enthalpy values of the dimerization were calculated from the temperature dependence of the thermodynamic equilibrium constant. On the basis of the results obtained, a method has been proposed so that the dimerization degree might be calculated for chosen values of ionic strength, temperature, and total concentration of methylene blue.

С помощью приложения теории сильных электролитов и статистических методов была охарактеризована зависимость концентрационной равновесной константы димеризации метиленового синего от ионной силы водных растворов неорганических электролитов, и были найдены значения термодинамической константы равновесия. На основе температурной зависимости термодинамической константы равновесия были рассчитаны величины энтальпии реакции димеризации. Исходя из полученных результатов, предлагается метод расчета степени димеризации при данных ионной силе, температуре и общей концентрации метиленового синего.

In the last decades a great deal of work has been devoted to the study of methylene blue aggregation. To a certain degree special position of this dyestuff results from some of its positive characteristics, such as rather simple method of synthesis known for a long time [1], easy purification, small molecules, and a considerable inclination to dimerization that is not accompanied by formation

of higher aggregates in relatively wide concentration region. A distinct and well observable spectrum in visible region that determines its characteristic deep-blue colour became in many cases a basis for the quantitative experimental investigation of the aggregation in solutions. That is why this compound is frequently used as a model in practical dyestuff chemistry. Theoretical molecular orbitals calculations elucidating the relationship between electronic structure of the compound and its physicochemical properties are also interesting [2—4].

The values of concentration equilibrium constant for the dimerization were mostly determined by spectroscopic measurements in aqueous media. In 1941 *Rabinowitch* and *Epstein* [5] determined $\log \{K_c\} = 3.55$ at $\theta = 20^\circ\text{C}$. Later in 1957 *Förster* and *König* [6] obtained the value of $\log \{K_c\} = 3.77$ at $\theta = 25^\circ\text{C}$. The spectroscopic studies of *Bergmann* and *O'Konski* carried out in the years 1963 and 1965 [7, 8] are in good agreement with this result. In 1965 *Hillson* and *McKay* [9] obtained $\log \{K_c\} = 4.4$ at temperature of 21°C by the polarographic method. However, the results of polarographic studies are affected by the high ionic strength of supporting electrolyte. Spectroscopic measurements of *Braswell* [10] in 1968 gave the value of $\log \{K_c\} = 3.3$ at $\theta = 30^\circ\text{C}$. In 1970 *Ballard* and *Park* [11] found out the value of $\log \{K_c\} = 3.81$ at $\theta = 20^\circ\text{C}$. The same value was obtained at $\theta = 25^\circ\text{C}$ by *Park*, *Yun*, and *Kim* [12]. An extensive contribution was published by *Fornilli*, *Sgroi*, and *Izzo* [13] in 1981, comprising the determination of the dimerization constants in aqueous solution of methylene blue for temperatures from 5°C to 30°C with the step of 5°C .

The spectroscopic study of the influence of inorganic electrolytes on the dimerization of methylene blue dyestuff has been the subject of the present paper. The temperature range was chosen so as to widen that of paper [13]. Since inorganic electrolytes represent the substantial constituents of dye baths and considerably influence technological procedure, we aimed at establishing quantitative relationship for the influence of inorganic electrolytes on the dimerization applying conclusions of the strong electrolytes theory [14].

Method

The calculation of concentration equilibrium constants for the dimerization is based on absorbance measurements at N_λ wavelengths λ_i ($i = 1, 2, \dots, N_\lambda$) in the region of the absorption doublet for a series of N_s solutions with different total concentration t_j ($j = 1, 2, \dots, N_s$) of methylene blue [15]. The concentration range is limited by the absorbance range of the used spectrophotometer.

If the concentrations of monomer and dimer in the j -th solution are denoted $c_{1,j}$ and $c_{2,j}$, respectively, the Lambert—Beer law for the absorbance ${}^1A_{i,j}$ at the wavelength λ_i per unitary cell width is written as

$${}^1A_{i,j} = A_{i,j}/d_j = \varepsilon_{i,1} c_{1,j} + \varepsilon_{i,2} c_{2,j} \quad (1)$$

where $\varepsilon_{i,1}$, $\varepsilon_{i,2}$ are molar absorption coefficients of the monomer and dimer, respectively, at the wavelength λ_i , and d_j is the cell width for the j -th solution. Including the material balance

$$t_j = c_{1,j} + 2c_{2,j} \quad (2)$$

eqn (1) takes the form

$${}^1A_{i,j} = (\varepsilon_{i,1} - 0.5\varepsilon_{i,2}) c_{1,j} + 0.5\varepsilon_{i,2} t_j \quad (3)$$

The concentration equilibrium constant of dimerization is defined by the expression

$$K_c = c_{2,j}/c_{1,j}^2 \quad (4)$$

With regard to the fact that both monomer and dimer are ions, K_c can be considered independent of t_j for a series of solutions with constant value of ionic strength that is determined by inorganic electrolyte. Combination of expressions (2) and (4) gives the equilibrium concentration of the monomer

$$c_{1,j} = (-1 + (1 + 8K_c t_j)^{1/2}) / 4K_c^{-1} \quad (5)$$

The best estimation of unknown values of concentration equilibrium constant and molar absorption coefficients can be obtained by minimization of the criterion function U having the form of weighed sum of squared deviations

$$U(K_c, \varepsilon_{1,1}, \dots, \varepsilon_{N,2}) = \sum_{i=1}^{N_\lambda} \sum_{j=1}^{N_s} w_{i,j} [\varepsilon_{i,1} c_{1,j} + \varepsilon_{i,2} c_{2,j} - {}^1A_{i,j}^{\text{obs}}]^2 \quad (6)$$

where ${}^1A_{i,j}^{\text{obs}}$ are experimental absorbance values, $A_{i,j}^{\text{obs}}$ redefined for unitary cell width and $w_{i,j}$ are weight coefficients. If the maximization of correlation coefficient for the measured and calculated values is required in calculation procedure the weight coefficients are defined by the expression

$$w_{i,j} = \kappa / ({}^1A_{i,j}^{\text{obs}})^2 \quad (7)$$

where the value of the constant κ follows from the normalization condition

$$\sum_{i=1}^{N_\lambda} \sum_{j=1}^{N_s} w_{i,j} = N_\lambda N_s \quad (8)$$

The minimization of the criterion function (6) with respect to the values of molar absorption coefficients leads for the chosen value of K_c to the system of two linear equations for each wavelength λ_i . The criterion function is also minimized with respect to the value of concentration equilibrium constant solving the system of linear equations for successively varied values of K_c .

The calculation of the estimate for the standard deviation of the concentration equilibrium constant logarithm $s(\log \{K_c\})$ is more complicated because of non-zero second-order mixed partial derivations of the criterion function with respect to equilibrium constant and individual molar absorption coefficients. A realistic estimation of the standard deviation can be obtained by a procedure that repeatedly adds errors produced by a random number generator with normal probability distribution to the experimental absorbance values. In this way prepared data sets afford the set of $\log \{K_c\}$ values from which the mean value and the standard deviation can be determined.

The thermodynamic equilibrium constant of dimerization is defined by the equation

$$K_a = \frac{a_{2,j}}{a_{1,j}^2} = \frac{c_{2,j} \gamma_{2,j}}{c_{1,j}^2 \gamma_{1,j}^2} = K_c \frac{\gamma_{2,j}}{\gamma_{1,j}^2} \quad (9)$$

where $a_{2,j}$, $a_{1,j}$ are activities of dimer and monomer in the j -th solution, respectively, and $\gamma_{2,j}$, $\gamma_{1,j}$ are the respective activity coefficients. The numerical value of K_a at given pressure and temperature depends only on the chosen standard state. In our case, the standard state has been represented by unimolar infinitely dilute solution. As the monomer and dimer of methylene blue are monovalent and bivalent cations, respectively, the values of their activity coefficients can be considered to be dependent only on the ionic strength of solution. For low values of ionic strength the limiting Debye—Hückel law can be applied [14, 16]

$$\log \gamma_{i,j} = -Az_i^2 I_j^{1/2} \quad i = 1, 2, \quad (10)$$

where A is a constant, $z_i = i$ is a charge number, and I_j is ionic strength of the j -th solution. Combining with eqn (9) the expression for the dependence of concentration equilibrium constant of dimerization on ionic strength is obtained

$$\log \{K_c\} = \log K_a + 2A I^{1/2} = \log K_a + b I^{1/2} \quad (11)$$

where b is a constant. Applying the regression analysis to the linear dependence $\log \{K_c\} = f(I^{1/2})$ obtained for the series of solutions with varied ionic strength the thermodynamic equilibrium constant of dimerization, constant b , and their standard deviations $s(\log K_a)$, $s(b)$ are determined. The standard deviation of approximation s_a and mean relative deviation of reproduction for the values of $\log \{K_c\}$ can be used to decide whether the submitted regression function suits our requirements

$$s_a^2 = \frac{1}{N_j - 2} \sum_{i=1}^{N_j} (\log \{K_{c,i}\} - \log K_a - b I_i^{1/2})^2 \quad (12)$$

$$\delta_r = 100 (\log \{K_{c,i}\} - \log K_a - b I_i^{1/2}) / \log \{K_{c,i}\} \quad (13)$$

$K_{c,i}$ is the concentration constant of dimerization determined from the spectra for a series of solutions with constant ionic strength I_i ($i = 1, 2, \dots, N_i$), $\bar{\delta}_r$ is calculated as a mean value of absolute values $|\delta_r|$.

Repeatedly used at varied thermodynamic temperatures this procedure leads to a dependence of K_a on temperature. The regression analysis of the linear function $\log K_a = f(1/T)$ renders values of standard reaction enthalpy ΔH_r° and its standard deviation $s(\Delta H_r^\circ)$ according to the reaction isobar equation and statistical characteristics s_a and $\bar{\delta}_r$ determined by a method analogous to the previous one.

Experimental

The standard preparation of the dyestuff methylene blue in the form of trihydrate of anal. grade purity (C. I. Basic Blue 9) was used in this study. It has been distributed by Lachema, Brno.

The solutions for measurements were prepared using redistilled water in the dye concentration range of 1×10^{-5} — 3×10^{-4} mol dm $^{-3}$. Seven constant values of ionic strength in the interval from 8.56×10^{-3} to 3.42×10^{-1} mol dm $^{-3}$ were adjusted applying alternatively NaCl and Na $_2$ SO $_4$ electrolytes.

The absorption spectra were measured by a double-beam registering spectrophotometer Specord UV VIS (Zeiss, Jena) in the wavelength region $\lambda = 540$ — 750 nm.

A thermocouple placed directly in measuring cell was used to registrate temperature of solutions. The absorbance measurements were carried out at $\theta = 24^\circ\text{C}$, 38°C , 47°C , and 55°C . The absorbance values were taken at eleven equidistant wavelength steps from the graphic registration of the spectra. The data-processing software has been written in the program language BASIC for personal computer HP 9830 A (Hewlett—Packard, USA).

Results and discussion

The concentration equilibrium constants of dimerization were calculated for solutions with different ionic strengths of both electrolytes at four temperatures using absorbances at 11 wavelengths for 8-membered concentration series. Results for electrolytes NaCl and Na $_2$ SO $_4$ are presented in Tables 1 and 2, respectively. The mean value of standard deviation for the values in Tables 1 and 2 is $s(\log \{K_c\}) \doteq 0.08$.

Figs. 1 and 2 show the dependences of $\log \{K_c\}$ on ionic strength at different temperatures. The straight lines obtained by regression analysis are depicted simultaneously. The results of linear regression analysis according to eqn (11) as $\log K_a$, coefficient b , their standard deviations $s(\log K_a)$, $s(b)$, standard deviation of approximation s_a and mean relative deviation $\bar{\delta}_r$ are given in Tables 3 and 4 for NaCl and Na $_2$ SO $_4$, respectively. Presented statistical characteristics in-

Table 1

Logarithms of concentration equilibrium constants of dimerization of methylene blue as a function of temperature at different ionic strengths of electrolyte NaCl

$\theta/^\circ\text{C}$	$I \cdot 10^2/(\text{mol dm}^{-3})$						
	0.856	1.71	3.42	5.13	8.56	17.1	34.2
24	3.838	3.903	3.918	3.748	3.798	4.178	4.408
38	3.578	3.518	3.598	3.578	3.668	3.798	4.028
47	3.598	3.398	3.448	3.438	3.578	3.678	3.968
55	3.278	3.288	3.368	3.458	3.528	3.503	3.796

Table 2

Logarithms of concentration equilibrium constants of dimerization of methylene blue as a function of temperature at different ionic strengths of electrolyte Na_2SO_4

$\theta/^\circ\text{C}$	$I \cdot 10^2/(\text{mol dm}^{-3})$						
	0.856	1.71	3.42	5.13	8.56	17.1	34.2
24	3.848	3.858	3.928	3.898	4.013	3.963	4.088
38	3.663	3.638	3.618	3.633	3.618	3.738	3.868
47	3.563	3.608	3.568	3.573	3.608	3.618	3.678
55	3.458	3.338	3.458	3.378	3.318	3.478	3.528

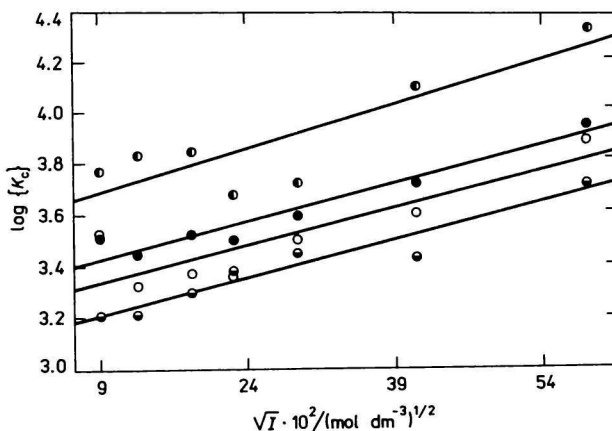


Fig. 1. Dependence of the concentration equilibrium constant of dimerization for methylene blue dyestuff on ionic strength in NaCl solutions at constant temperatures. ● 24°C; ● 38°C; ○ 47°C; ● 55°C.

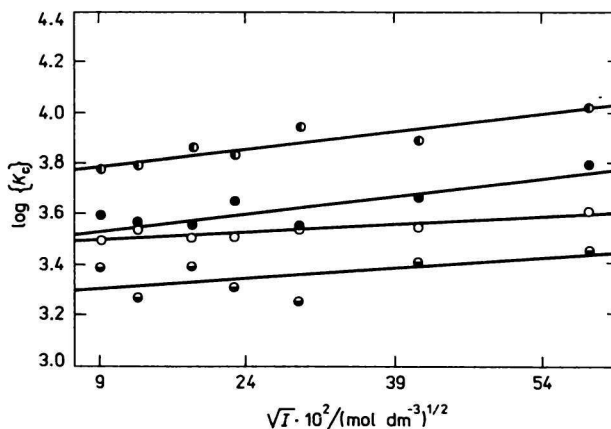


Fig. 2. Dependence of the concentration equilibrium constant of dimerization for methylene blue dyestuff on ionic strength in Na_2SO_4 solutions at constant temperatures. The denotation is the same as in Fig. 1.

dicating satisfactory precision of $\log K_a$ values determined in this way, while the coefficient b is affected by dispersion of $\log \{K_c\}$ values around the regression straight line. The data for solutions with NaCl at $\theta = 24^\circ\text{C}$ give the worst regression fit with $s(\log K_a) = 0.1$ and $s_a = 0.14$. This situation is due to a great negative deviation of two $\log \{K_c\}$ values (Fig. 1) that might be caused by experimental errors. In other cases, the values of $\log \{K_c\}$ are rather uniformly dispersed around the regression straight lines. That is the reason why more complex expressions that would be more suited for the ionic strength region could not be applied to the relationship between activity coefficients and ionic strength.

Comparison of the results obtained by different authors at different temperatures is presented in the coordinate system of $\log \{K_c\}$ vs. $1/T$ in Fig. 3, so the differences between the results are clearly shown.

Table 3

Linear regression analysis of the dependence of the logarithm of concentration equilibrium constant of dimerization on \sqrt{I} for electrolyte NaCl

$\theta/^\circ\text{C}$	$\log K_a$	$s(\log K_a) \cdot 10^2$	$\frac{b}{\text{dm}^{3/2} \text{mol}^{-1}}$	$\frac{10^2 \cdot s(b)}{\text{dm}^{3/2} \text{mol}^{-1}}$	$s_a \cdot 10^2$	$\frac{\delta_r}{\%}$
24	3.648	10.2	1.17	31.98	13.6	2.6
38	3.408	3.75	0.99	11.77	3.8	1.0
47	3.318	8.21	0.98	25.79	10.9	2.2
55	3.188	4.16	0.99	13.07	5.6	1.0

Table 4

Linear regression analysis of the dependence of the logarithm of concentration equilibrium constant of dimerization on \sqrt{I} for electrolyte Na_2SO_4

$\theta/^\circ\text{C}$	$\log K_a$	$s(\log K_a)$	$10^2 \frac{b}{\text{dm}^{3/2} \text{mol}^{-1}}$	$\frac{10^2 s(b)}{\text{dm}^{3/2} \text{mol}^{-1}}$	10^2	$\frac{\delta_r}{\%}$
24	3.814	2.89	0.46	9.08	4.9	0.7
38	3.558	3.84	0.457	12.06	5.1	1.1
47	3.547	1.5	0.20	4.43	2.1	0.4
55	3.347	5.67	0.292	17.82	7.6	1.6

If the value $\log \{K_c\} = 4.4$, obtained by polarographic measurements at $\theta = 20^\circ\text{C}$ and at high ionic strength of supporting electrolyte [9], is not taken into account while analyzing the results we can say the other values obtained spectrophotometrically are in rather good agreement except the results of *Rabinowitch and Epstein* [5] and *Braswell* [10]. It is worth noticing that the result depends not only on the used method but also on the investigated concentration region, ionic strength, and data evaluation method. In the previous works statistical methods were not usually applied.

If the values of $\log \{K_c\}$ obtained by other authors in solutions without inorganic electrolytes, *i.e.* at a very low ionic strength, are identified with the values of $\log K_a$, they may be compared with $\log K_a$ obtained in this work. Comparison of the results in Tables 3 and 4 with those in Fig. 3 leads to a

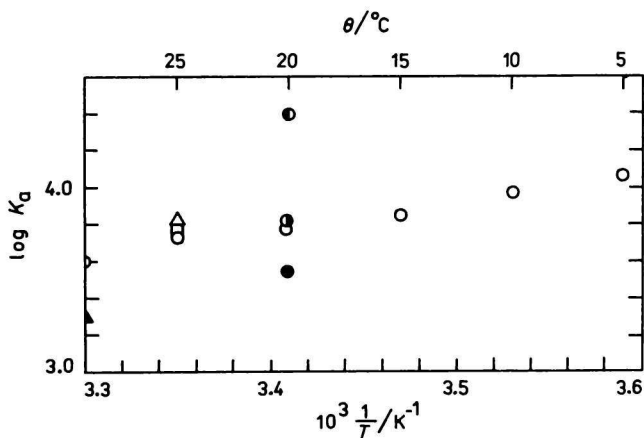


Fig. 3. Values of equilibrium constant for methylene blue dimerization published in other papers. \circ [13]; \bullet [5]; \circ [9]; \square [11]; \triangle [12]; \blacktriangle [10]; \square [6–8].

Table 5

 Regression analysis of the temperature dependence of the logarithm of thermodynamic equilibrium constant of dimerization for constant ΔH_r°

$\theta/^\circ\text{C}$	$\log K_a$	$\log K_a^{\text{calc}}$	$\delta_r/\%$	$\frac{\Delta H_r^\circ}{\text{kJ mol}^{-1}}$	$\frac{s(\Delta H_r^\circ)}{\text{kJ mol}^{-1}}$	s_a	$\delta_r^\circ/\%$
NaCl							
24	3.648	3.642	-0.17				
38	3.408	3.428	0.57	-27.08	0.08	0.02	0.36
47	3.318	3.300	-0.55				
55	3.188	3.192	0.13				
Na ₂ SO ₄							
24	3.814	3.807	-0.19				
38	3.558	3.602	1.22	-25.90	0.26	0.06	1.06
47	3.547	3.480	-1.93				
55	3.347	3.377	0.88				
Ø(NaCl + Na ₂ SO ₄)							
24	3.731	3.724	-0.19				
38	3.483	3.515	0.92	-26.49	0.32	0.11	0.71
47	3.433	3.390	-1.25				
55	3.268	3.284	0.49				

conclusion that the calculated values of $\log K_a$ are in good agreement with the results published in paper [13] and represent an extension of them towards higher temperatures.

The results of regression analysis for the thermodynamic equilibrium constant dependence on temperature are presented in Table 5. Simultaneously, the average $\log K_a$ values for different electrolytes at the same temperature are given. The results indicate statistically more significant description of the dependence for NaCl electrolyte. However, the obtained standard reaction enthalpies may be said to have practically equal values in the range of their standard deviations. The resulting mean value $\Delta H_r^\circ = -26.5 \text{ kJ mol}^{-1}$ is somewhat lower than the values $-22.61 \text{ kJ mol}^{-1}$, $-24.7 \text{ kJ mol}^{-1}$, and $-22.57 \text{ kJ mol}^{-1}$ presented in papers [17–19]. On the other hand, after careful treatment of experimental data *Fornilli et al.* obtained the value of $-28.05 \text{ kJ mol}^{-1}$ for the temperature region from 5°C to 30°C . The diagram of $\log K_a$ vs. $1/T$ presented in paper [13] indicates the increase of standard reaction enthalpy with temperature. This fact has been confirmed by numerical evaluation. The value of $\Delta H_r^\circ = -32.21 \text{ kJ mol}^{-1}$ has been obtained for the temperature region $5\text{--}15^\circ\text{C}$ while $\Delta H_r^\circ = -28.86 \text{ kJ mol}^{-1}$ for the interval $20\text{--}30^\circ\text{C}$. Therefore the joined

Table 6

Regression analysis of the temperature dependence of the logarithm of thermodynamic equilibrium constant of dimerization for ΔH_r° linearly dependent on temperature
(Data from paper [13], * data obtained by us)

$\theta/^\circ\text{C}$	$\log K_a$	$\log K_a^{\text{calc}}$	$\delta_r/\%$	$\frac{-\Delta H_r^\circ(T)}{\text{kJ mol}^{-1}}$	$\frac{s(\Delta H_r^\circ(T))}{\text{kJ mol}^{-1}}$
5	4.08	4.08	-0.08	30.1	2.8
10	3.98	3.98	-0.06	29.6	2.3
15	3.87	3.88	0.36	29.0	1.8
20	3.79	3.79	0.13	28.5	1.3
25	3.73	3.71	-0.52	27.9	1.0
30	3.62	3.63	0.29	27.4	0.9
24*	3.73	3.73	-0.10	28.0	1.0
38*	3.48	3.51	0.81	26.5	1.4
47*	3.43	3.39	-1.30	25.5	2.3
55*	3.27	3.29	0.63	24.6	3.1

$$s_a = 0.024$$

$$\delta_r = 0.43 \%$$

set of the data from paper [13] and the mean values of $\log K_a$ of this work were treated assuming linear dependence of the standard reaction enthalpy on temperature in the region from 5 °C to 55 °C

$$\Delta H_r^\circ(T) = \Delta H_r^\circ(T_0) + \Delta \bar{C}_{p,r}^\circ(T - T_0) \quad (14)$$

where $\Delta \bar{C}_{p,r}^\circ$ is the mean value of the standard reaction heat capacity at constant pressure in the temperature region studied. The standard reaction enthalpy dispersion value at temperature T has been calculated from the dispersions $s^2(\Delta H_r^\circ(T_0))$, $s^2(\Delta \bar{C}_{p,r}^\circ)$ and the covariance $\text{cov}(\Delta H_r^\circ(T_0), \Delta \bar{C}_{p,r}^\circ)$

$$s^2(\Delta H_r^\circ(T)) = s^2(\Delta H_r^\circ(T_0)) + T^2 s^2(\Delta \bar{C}_{p,r}^\circ) + 2T \text{cov}(\Delta H_r^\circ(T_0), \Delta \bar{C}_{p,r}^\circ) \quad (15)$$

As follows from the results of regression analysis presented in Table 6, the value of standard reaction enthalpy increases in the studied temperature region from $-30.1 \text{ kJ mol}^{-1}$ at $\theta = 5^\circ\text{C}$ to $-24.6 \text{ kJ mol}^{-1}$ at $\theta = 55^\circ\text{C}$. Nevertheless, the statistical significance of this trend is small.

The presented statistical evaluation should result in the possibility of theoretical prediction of monomer—dimer equilibrium state at a certain temperature and ionic strength. According to eqn (11) constant A of the limiting Debye—Hückel law equals $1/2 b$ where b is the derivative of concentration equilibrium constant logarithm with respect to the square root of ionic strength. With regard to great standard deviations $s(b)$ (Tables 3 and 4) the results obtained may be

stated not to contradict theoretical values of the constant A (in case of NaCl electrolyte they are even in full harmony). For practical use the values of A can be calculated from the theoretical relationship.

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