

Effect of Temperature on UV Spectra of Concentrated NaNO_3 Aqueous Solutions*

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RECEIVED DECEMBER 12, 2006; REVISED JULY 12, 2007; ACCEPTED JULY 16, 2007

The effect of temperature on the $\pi^* \leftarrow n$ transition band of nitrate ion in NaNO_3 aqueous solutions ($0.2 \leq c/\text{mol dm}^{-3} \leq 4.2$) was studied in the temperature range (15–70) °C, $\Delta\theta = 5$ °C. For each solution, the spectral maximum at ≈ 300 nm was found to shift bathochromically with increasing temperature, and a well-defined isosbestic point occurred. Accordingly, the result of principal-components analysis (PCA) of the corresponding spectral matrices was the effective rank (pseudorank) of 2 in all cases. The spectral changes were proven to be reversible. Recently, it has been shown that two forms of 'free' nitrate ion ($\alpha\text{-NO}_3^-$ and $\beta\text{-NO}_3^-$) are present in dilute aqueous solutions differing in the structure of the hydration shells. Since in solutions with higher electrolyte concentrations the two forms can be expected to form ion pairs, four equilibrium reactions were assumed to take place – interconversion between free nitrate forms, ion-pairing reactions of $\alpha\text{-NO}_3^-$ and $\beta\text{-NO}_3^-$, and interconversion between the ion pairs $\{\text{Na}^+(\alpha\text{-NO}_3^-)\}$ and $\{\text{Na}^+(\beta\text{-NO}_3^-)\}$. It was shown that the observed spectral changes caused by change in temperature could be explained if the ion-pairing reactions were taken to be approximately temperature independent (*i.e.* the corresponding $\Delta_r H \approx 0$). The spectrum of $\text{NaNO}_3(\text{aq})$ solution could be expressed as a linear combination of two temperature independent 'hybrid' spectra. That could explain the results of PCA as well as the existence of the isosbestic point over the entire temperature range examined.

Keywords

UV spectrometry
temperature effect
sodium nitrate
ion association
principal-components analysis
van't Hoff equation

INTRODUCTION

In previous papers^{1,2} we described the effect of temperature on the $\pi^* \leftarrow n$ and $\pi^* \leftarrow \pi$ transition bands of nitrate ion in dilute aqueous solutions (NaNO_3 , KNO_3 , NMe_4NO_3). The $\pi^* \leftarrow n$ transition band was found to be temperature dependent, and the occurrence of two well-defined isosbestic points was observed.¹ In addition, the spectral changes caused by change in temperature were reversible and cation independent. From these findings the existence

of an equilibrium between two spectrally distinct nitrate species was deduced. By assuming the constancy of interconversion reaction enthalpy in the examined temperature range (10–70 °C), it was possible to estimate the interconversion equilibrium constants at different temperatures which, in turn, enabled us to estimate the corresponding reaction enthalpy and entropy by means of van't Hoff plots. The obtained data led to the hypothesis that two nitrate forms differed in the hydrogen-bonding structure of their hydration shells.

* Dedicated to Professor Nikola Kallay on the occasion of his 65th birthday.

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TABLE I. Positions of maxima and minima, λ_{\max}/nm (λ_{\min}/nm in parentheses), in $\text{NO}_3^-(\text{aq})$ spectra for selected temperatures and electrolyte concentrations

$c/\text{mol dm}^{-3}$	15 °C		25 °C		50 °C		70 °C	
0.2	301.0	(262.0)	301.5	(262.5)	302.0	(263.5)	303.0	(264.5)
2.0	300.5	(261.5)	301.0	(262.0)	301.5	(263.0)	302.0	(264.0)
3.4	300.0	(261.5)	300.5	(262.0)	301.0	(263.0)	301.5	(264.0)
4.2	300.0	(261.5)	300.0	(262.0)	300.5	(263.0)	300.5	(263.5)

This work is focused on the study of temperature dependence of the UV spectra of aqueous NaNO_3 solutions at higher salt concentrations where ion association (detectable by UV absorption spectrometry³) is expected to take place. The existence of two forms of 'free' nitrate ions makes the speciation in the investigated systems rather complex, since both forms can be expected to form associated ion pairs with sodium cations. Consequently, several equilibria are likely to exist in the solutions. An attempt has been made to explain the observed spectral changes by taking those equilibria into account.

EXPERIMENTAL

Sodium nitrate, originally of analytical reagent grade, was dried to constant mass and then dissolved in bidistilled water. The range of NaNO_3 concentrations in thus prepared series of solutions was $0.2 \leq c/\text{mol dm}^{-3} \leq 4.2$. The absorption spectra of the solutions (wavelength range $250 \leq \lambda/\text{nm} \leq 350$, sampling interval 0.5 nm) were recorded by means of a Varian Cary 5 UV-Vis-NIR double-beam spectrometer (absorbance readability ± 0.0001 , wavelength reproducibility ± 0.025 nm) equipped with a thermostating device (precision ± 0.1 °C). Spectra of all solutions were recorded at 12 different temperatures, ranging from 15 °C to 70 °C. Quartz cells (1 or 10 mm) were used throughout. The parts of spectra where absorbance exceeded 3.0 were discarded.

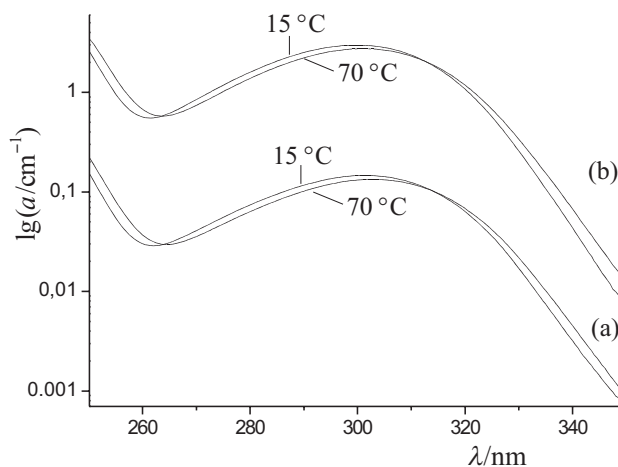


Figure 1. UV absorption spectra of $\text{NaNO}_3(\text{aq})$ ($\pi^* \leftarrow n$ transition): (a) $c_{\min} = 0.2 \text{ mol dm}^{-3}$, (b) $c_{\max} = 4.2 \text{ mol dm}^{-3}$.

RESULTS AND DISCUSSION

Comparison of Raw Spectra

It is well known that UV absorption spectrum of $\text{NO}_3^-(\text{aq}, \infty)$ consists of two bands. One of them (corresponding to the $\pi^* \leftarrow \pi$ transition) is a highly intensive peak at approximately 200 nm with the absorption coefficient $\varepsilon = 9750 \text{ cm}^2 \text{ mmol}^{-1}$. The other peak, centered at ≈ 300 nm, is much weaker ($\varepsilon \approx 7 \text{ cm}^2 \text{ mmol}^{-1}$); it is assigned to the $\pi^* \leftarrow n$ transition. The absorption minimum near 264 nm is a result of their partial overlap.¹⁻⁶

The absorption spectra of sodium nitrate aqueous solutions, recorded at the lowest (a) and highest (b) electrolyte concentrations, at two extreme temperatures (15 °C and 70 °C), are shown in Figure 1 (the spectra are normalised by dividing by the length of optical path: $a = A/l$).

The shifts of the spectra caused by changes in either salt concentration or temperature are clearly visible. The effects of the temperature and salt concentration on the peak wavelength, λ_{\max} , and the position of spectral minimum, λ_{\min} , are easier to discern by inspecting Table I where a few characteristic data points are shown.

The temperature increase from 15 °C to 70 °C caused slight *bathochromic* shifts of both the absorption maximum and minimum. On the other hand, the concentration change from 0.2 mol dm^{-3} to 4.2 mol dm^{-3} caused *hypsochromic* shifts of both the absorption maximum and minimum. Although rather small ($\Delta\lambda \leq 2$ nm), these shifts proved to be regular and reproducible, owing to the high precision of the spectrometer. The reversibility of spectral shifts was confirmed experimentally.

Looking at Figure 1, one can see a well-defined isosbestic point at 264 nm, as well as another (less certain) isosbestic point in the range between 312 nm and 317 nm. Because of the steepness of the spectral curve, it is spread out, forming an isosbestic region. As generally known, the existence of the isosbestic point indicates an equilibrium between two spectrally distinct species. An additional evidence for this is the reversibility of the spectral changes.

Principal-components Analyses

For each electrolyte concentration, the spectral matrix consisting of UV spectra recorded at 12 different tempe-

TABLE II. Principal-components analysis of UV spectra of NaNO₃(aq) at constant concentration, $c = 2.8 \text{ mol dm}^{-3}$; $15 \leq \theta/^\circ\text{C} \leq 70$ (dim = 201×12).

$k^{(a)}$	$R_0^{(b)}$	$P(R_0)^{(c)}$
1	0.998806	< 0.00001
<u>2</u>	0.048816	<u>0.008266</u>
3	0.001926	0.462
4	0.000174	0.497
5	0.000093	0.498
...
12	0.000042	0.499

(a) k : ordinal number of the component

(b) R_0 : data/component correlation coefficient

(c) $P(R_0)$: significance level; the last significant value is underlined

tures was subjected to principal-components analysis, PCA (the method and R_0 rank determinant are described elsewhere⁷). As an example, the results obtained for an arbitrarily selected concentration of NaNO₃ (aq, $c = 2.8 \text{ mol dm}^{-3}$) are given in Table II.

If the R_0 test is applied at the customary significance level of $P(R_0) = 0.05$, it can be seen that the effective rank (pseudorank) is 2. (Note the approximate constancy of $P(R_0) \approx 0.5$ for residual components.) The same effective rank was found for all other concentrations. Together with the experimentally observed reversibility of spectral changes, as well as the existence of isosbestic points, the above results indicate the existence of *at least* two spectrally different species in all systems examined. However, as already mentioned, the increase of salt concentration in isothermal experiments caused a slight shift of the nitrate UV band towards shorter wavelengths at all temperatures examined. The PCA of the corresponding spectral matrices again indicated the presence of two spectrally active species in the experimental concentration range. An example of PCA of isothermal data is given in Table III.

TABLE III. Principal-components analysis of UV spectra of NaNO₃(aq, $0.2 \leq c/\text{mol dm}^{-3} \leq 4.2$) at constant temperature, $\theta = 25^\circ\text{C}$; (dim = 201×13)

$k^{(a)}$	$R_0^{(b)}$	$P(R_0)^{(c)}$
1	0.998545	< 0.00001
<u>2</u>	0.053884	<u>0.004074</u>
3	0.001930	0.462
4	0.000272	0.495
5	0.000212	0.496
...
12	0.000050	0.499

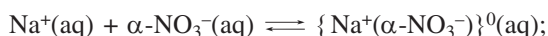
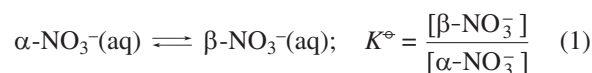
(a) k – ordinal number of the component

(b) R_0 – data/component correlation coefficient

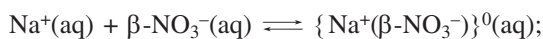
(c) $P(R_0)$ – significance level; the last significant value is underlined

Speciation

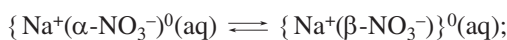
Two species detected in isothermal experiments can be thought of as the 'free' nitrate ion and the $\{\text{NaNO}_3\}^0$ associated ion pair. However, it has been shown¹ that in dilute aqueous solutions of nitrate, where ionic association cannot be observed, there are two forms of 'free' nitrate ion, *viz.* $\alpha\text{-NO}_3^-$ and $\beta\text{-NO}_3^-$, differing in the structures of the hydration shells. At higher concentrations, both nitrate entities could be expected to form ion pairs with sodium cation. Accordingly, four equilibria are possible:



$$K_{M\alpha} = \frac{[\{\text{Na}^+(\alpha\text{-NO}_3^-)\}^0]}{[\text{Na}^+][\alpha\text{-NO}_3^-]} \quad (2)$$



$$K_{M\beta} = \frac{[\{\text{Na}^+(\beta\text{-NO}_3^-)\}^0]}{[\text{Na}^+][\beta\text{-NO}_3^-]} \quad (3)$$



$$K_a^\ominus = \frac{[\{\text{Na}^+(\beta\text{-NO}_3^-)\}^0]}{[\{\text{Na}^+(\alpha\text{-NO}_3^-)\}^0]} \quad (4)$$

where [...] denotes equilibrium concentrations of the species in solution.

Eq. (1) defines the standard equilibrium constant of interconversion of two forms of 'free' nitrate ion. The values of this constant at different temperatures, as well as standard conversion enthalpy and entropy (from van't Hoff plots) were reported previously.¹

Eqs. (2) and (3) define stoichiometric (concentration) constants for the association of sodium cation with α - and β -forms of nitrate ion, respectively.

The equilibrium constant for the interconversion of the associated forms of nitrate ion, defined by Eq. (4) as the concentration ratio of two electroneutral species, should be nearly equal to the standard equilibrium constant. By introducing Eqs. (2) and (3) into (4) it can be seen that K_a^\ominus does not depend on the salt concentration:

$$K_a^\ominus(T) = \frac{[\{\text{Na}^+(\beta\text{-NO}_3^-)\}^0]}{[\{\text{Na}^+(\alpha\text{-NO}_3^-)\}^0]} = \frac{K_{M\beta}(c,T)[\text{Na}^+][\beta\text{-NO}_3^-]}{K_{M\alpha}(c,T)[\text{Na}^+][\alpha\text{-NO}_3^-]} = \frac{K_{M\beta}(c,T)}{K_{M\alpha}(c,T)} \cdot K^\ominus(T) \quad (5)$$

Upon replacing stoichiometric association constants, $K_{M\alpha}$ and $K_{M\beta}$, by corresponding standard equilibrium constants, Eq. (5) becomes:

$$K_a^\circ(T) = \frac{K_{M\beta}^\circ(T)}{K_{M\alpha}^\circ(T)} \cdot \frac{\gamma(\beta\text{-NO}_3^-) \cdot \gamma(\{\text{Na}^+(\beta\text{-NO}_3^-)\}^0)}{\gamma(\alpha\text{-NO}_3^-) \cdot \gamma(\{\text{Na}^+(\alpha\text{-NO}_3^-)\}^0)} \cdot K(T) \quad (6)$$

Since $\gamma(\alpha\text{-NO}_3^-)$ and $\gamma(\beta\text{-NO}_3^-)$ are approximately equal¹ Eq. (6) is reduced to:

$$K_a^\circ(T) = \frac{K_{M\beta}^\circ(T)}{K_{M\alpha}^\circ(T)} \cdot K^\circ(T) \quad (7)$$

The experimental data and PCA results (effective rank = 2) suggest that only the concentration ratio of the 'mixtures' (*i.e.* $\alpha\text{-NO}_3^- + \{\text{Na}^+(\alpha\text{-NO}_3^-)\}^0$ and $\beta\text{-NO}_3^- + \{\text{Na}^+(\beta\text{-NO}_3^-)\}^0$) changes with temperature. This change should be similar to the 'isomerisation' of nitrate ion in dilute aqueous solutions.¹ The ratio is defined by the following expression:

$$r(c, T) = \frac{[\{\text{Na}^+(\beta\text{-NO}_3^-)\}^0] + [\beta\text{-NO}_3^-]}{[\{\text{Na}^+(\alpha\text{-NO}_3^-)\}^0] + [\alpha\text{-NO}_3^-]} = \frac{c_\beta}{c_\alpha} = \frac{x}{1-x} \quad (8)$$

where x denotes the degree of conversion from mixture ($\alpha\text{-NO}_3^-$, $\{\text{Na}^+(\alpha\text{-NO}_3^-)\}^0$) to mixture ($\beta\text{-NO}_3^-$, $\{\text{Na}^+(\beta\text{-NO}_3^-)\}^0$):

$$x(T) = \left(\frac{c_\beta}{c} \right)_T \quad (9)$$

(c is the total salt concentration). Thus, the $r(c, T)$ ratio in Eq. (8) is uniquely determined by x and *vice versa*. If the effect of temperature on the investigated systems is similar to that observed in dilute aqueous nitrate solutions, the plot of $\ln r$ vs. $1/T$ should be linear:¹

$$\ln r(c, T) = -\frac{\Delta_r H}{RT} + \frac{\Delta_r S}{R} \quad (10)$$

Besides, the values of $\Delta_r H$ and $\Delta_r S$ can be expected to be similar to those obtained for dilute aqueous solutions of nitrate ion.

Computations

The spectra of solutions, sorted in the ascending order of temperatures T_j ($j = 1, \dots, J$), were arranged into the data matrix, $\mathbf{A} = [a_{ij}] = [A_{ij} / I]$ as column vectors, one for each solution (a_{ij} denotes the value of a measured at wavelength λ_i ($i = 1, \dots, I$)). According to Beer's law, the data matrix can be represented by relation:

$$\mathbf{A} = \mathbf{E} \cdot \mathbf{C} \quad (11)$$

where \mathbf{E} stands for the matrix of absorption coefficients, and \mathbf{C} represents concentration profiles. The matrices \mathbf{E}

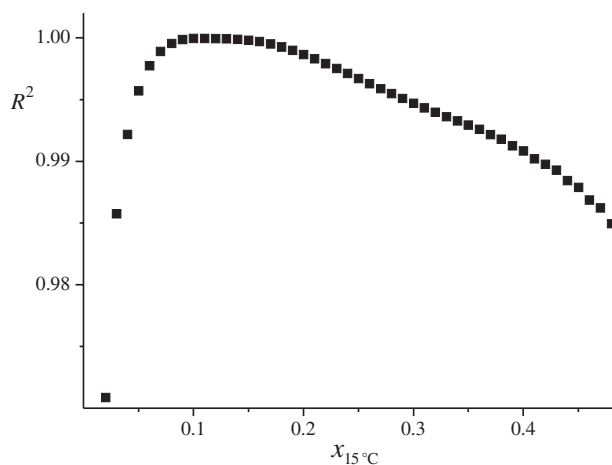


Figure 2. Maximization of R^2 for $\text{NaNO}_3(\text{aq}, c = 2.8 \text{ mol dm}^{-3})$; $R_{\text{max}}^2 = 0.99988$, degree of conversion: $x = 0.901$.

and \mathbf{C} can be estimated by using the algorithm described in more detail earlier.¹

The algorithm is aimed at finding the concentration profiles which maximize the coefficient of determination, R^2 , for the least-squares fit of Eq. (10). The solutions are subject to the following constraints:

- Non-negativity of absorption coefficients and concentrations,
- Constancy of total nitrate amount: $n(\alpha\text{-NO}_3^- + \{\text{Na}^+(\alpha\text{-NO}_3^-)\}^0) + n(\beta\text{-NO}_3^- + \{\text{Na}^+(\beta\text{-NO}_3^-)\}^0) = n_{\text{tot}}$,
- Monotonic increase of x with increasing temperature.

The unknown absorption coefficients (matrix \mathbf{E} of $(\alpha\text{-NO}_3^- + \{\text{Na}^+(\alpha\text{-NO}_3^-)\}^0)$ and $(\beta\text{-NO}_3^- + \{\text{Na}^+(\beta\text{-NO}_3^-)\}^0)$) were estimated from the spectra recorded at 15 °C and 70 °C for each pair of assumed values of $x(15 \text{ °C})$ and $x(70 \text{ °C})$. The corresponding concentration matrices were then computed by means of equation:

$$\mathbf{C} = \mathbf{A} \cdot (\mathbf{E}^T \cdot \mathbf{E})^{-1} \cdot \mathbf{E}^T \quad (12)$$

From the obtained concentrations of $(\alpha\text{-NO}_3^- + \{\text{Na}^+(\alpha\text{-NO}_3^-)\}^0)$ and $(\beta\text{-NO}_3^- + \{\text{Na}^+(\beta\text{-NO}_3^-)\}^0)$ the values of r at different temperatures were calculated for each assumed $\{x(15 \text{ °C}), x(70 \text{ °C})\}$ pair. Dependence of $\ln r$ on $1/T$ was fitted according to Eq. (10) and the corresponding R^2 value was computed. An example of the course of R^2 maximization ($\text{NaNO}_3, \text{aq}, c = 2.8 \text{ mol dm}^{-3}$; $\vartheta = 15 \text{ °C}$) is given in Figure 2. The van't Hoff plot corresponding to the maximal R^2 is shown in Figure 3.

As can be seen from the data in Table IV, the degree of conversion of $(\alpha\text{-NO}_3^- + \{\text{Na}^+(\alpha\text{-NO}_3^-)\}^0)$ into $(\beta\text{-NO}_3^- + \{\text{Na}^+(\beta\text{-NO}_3^-)\}^0)$,

$$x = \frac{r(c, T)}{1 + r(c, T)} \quad (13)$$

remains rather low in the whole temperature range, ranging from ≈ 0.09 at 15 °C to ≈ 0.21 at 70 °C for the lowest electrolyte concentration, $c = 0.2 \text{ mol dm}^{-3}$, while for the highest concentration, $c = 4.2 \text{ mol dm}^{-3}$, the x values range from ≈ 0.1 at 15 °C to ≈ 0.22 at 70 °C.

Estimated Equilibrium Parameters

By looking at rows in Table IV ($\vartheta = \text{const.}$) one can notice that:

$$r(c, T) \approx r(T) \quad (14)$$

The $\Delta_r H$ and $\Delta_r S$ values are very similar to those obtained for NO₃⁻(aq, ∞) solutions.¹ We can therefore conclude that the temperature dependences of r and K^\ominus are similar. It is interesting to examine at what conditions the two dependences will be equal. The ratio r in Eq. (8) can be written as:

$$r = \frac{[\{\text{Na}^+(\beta\text{-NO}_3^-)\}^0] + [\beta\text{-NO}_3^-]}{[\{\text{Na}^+(\alpha\text{-NO}_3^-)\}^0] + [\alpha\text{-NO}_3^-]} = \frac{K_{M\beta}[\text{Na}^+][\beta\text{-NO}_3^-] + [\beta\text{-NO}_3^-]}{K_{M\alpha}[\text{Na}^+][\alpha\text{-NO}_3^-] + [\alpha\text{-NO}_3^-]} \quad (15)$$

where equilibrium concentrations $[\{\text{Na}^+(\alpha\text{-NO}_3^-)\}^0]$ and $[\{\text{Na}^+(\beta\text{-NO}_3^-)\}^0]$ are expressed using appropriate association constants $K_{M\alpha}$ and $K_{M\beta}$ (Eqs. (2) and (3)), respectively. If $[\beta]$ and $[\alpha]$ are expressed by means of Eq. (1), the following relation is obtained:

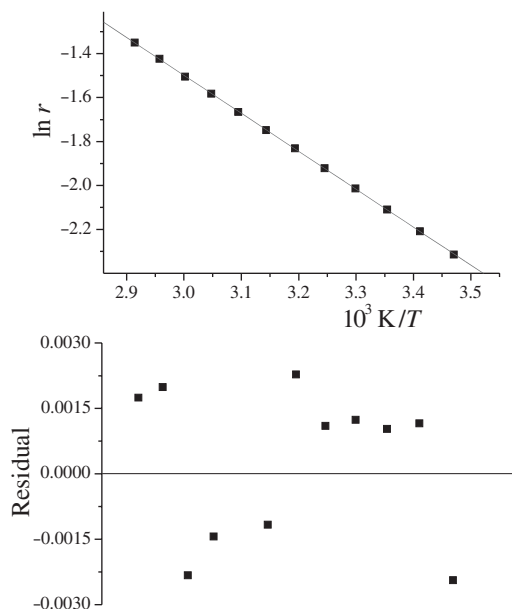


Figure 3. Van't Hoff and residual plots for reversible ($\alpha\text{-NO}_3^-$, $\{\text{Na}^+(\alpha\text{-NO}_3^-)\}^0 \rightleftharpoons \beta\text{-NO}_3^-$, $\{\text{Na}^+(\beta\text{-NO}_3^-)\}^0$) interconversion of NaNO₃(aq, $c = 2.8 \text{ mol dm}^{-3}$).

$$r = K^\ominus \cdot \frac{K_{M\beta}[\text{Na}^+] + 1}{K_{M\alpha}[\text{Na}^+] + 1} \quad (16)$$

By differentiating the logarithm of this expression with respect to temperature, it follows:

$$\frac{\partial \ln r}{\partial T} = \frac{\partial \ln K^\ominus}{\partial T} + \frac{\partial \ln(K_{M\beta}[\text{Na}^+] + 1)}{\partial T} - \frac{\partial \ln(K_{M\alpha}[\text{Na}^+] + 1)}{\partial T} \quad (17)$$

and after rearranging:

$$\frac{\partial \ln r}{\partial T} = \frac{\partial \ln K^\ominus}{\partial T} + \frac{1}{K_{M\beta}[\text{Na}^+] + 1} \left(\frac{\partial K_{M\beta}}{\partial T} [\text{Na}^+] + \frac{\partial [\text{Na}^+]}{\partial T} K_{M\beta} \right) - \frac{1}{K_{M\alpha}[\text{Na}^+] + 1} \left(\frac{\partial K_{M\alpha}}{\partial T} [\text{Na}^+] + \frac{\partial [\text{Na}^+]}{\partial T} K_{M\alpha} \right) \quad (18)$$

From Eq. (18) it is obvious that the equality

$$\frac{\partial \ln r}{\partial T} = \frac{\partial \ln K^\ominus}{\partial T} \quad (19)$$

holds if either of the following relations is true:

$$\mathbf{a} \quad K_{M\alpha} = K_{M\beta} \text{ and } \frac{\partial K_{M\alpha}}{\partial T} = \frac{\partial K_{M\beta}}{\partial T} \quad (20)$$

or

$$\mathbf{b} \quad \frac{\partial K_{M\alpha}}{\partial T} \approx \frac{\partial K_{M\beta}}{\partial T} \approx 0 \quad (21)$$

Since conditions **a** are less likely to be fulfilled, the similarity of temperature dependence of r and K^\ominus could be explained by assuming that the constants $K_{M\alpha}$ and $K_{M\beta}$ are approximately temperature independent (condition **b**), i.e. $\Delta_{(2)}H \approx \Delta_{(3)}H \approx 0$.

These findings are in accordance with the occurrence of isobestic points in the experimental spectra, and with the PCA results. Although in the examined solutions there are four spectrally different species ($\alpha\text{-NO}_3^-$, $\{\text{Na}^+(\alpha\text{-NO}_3^-)\}^0$, $\beta\text{-NO}_3^-$, $\{\text{Na}^+(\beta\text{-NO}_3^-)\}^0$), at any wavelength the absorbance can be expressed as a linear combination of two variables:

$\forall T$:

$$\begin{aligned} a(\lambda, c) = & \varepsilon_\alpha(\lambda)[\alpha\text{-NO}_3^-] + \varepsilon_{M\alpha}(\lambda)K_{M\alpha}[\text{Na}^+][\alpha\text{-NO}_3^-] + \\ & \varepsilon_\beta(\lambda)[\beta\text{-NO}_3^-] + \varepsilon_{M\beta}(\lambda)K_{M\beta}[\text{Na}^+][\beta\text{-NO}_3^-] = \\ & [\alpha]\{\varepsilon_\alpha(\lambda) + \varepsilon_{M\alpha}(\lambda)K_{M\alpha}[\text{Na}^+]\} + [\beta]\{\varepsilon_\beta(\lambda) + \\ & \varepsilon_{M\beta}(\lambda)K_{M\beta}[\text{Na}^+]\} \quad (22) \end{aligned}$$

TABLE IV. Ratio r , enthalpies and entropies of reversible (α -NO₃⁻, {Na⁺(α -NO₃⁻)⁰} \rightleftharpoons β -NO₃⁻, {Na⁺(β -NO₃⁻)⁰}) conversion, 0.2 $\leq c/\text{mol dm}^{-3} \leq 4.2$

$\theta/^\circ\text{C}$	r																
	0.2	0.6	0.8	1.2	1.6	2.0	2.4	2.8	3.4	3.6	3.8	4.0	4.2				
15	0.099	0.117	0.114	0.120	0.119	0.110	0.104	0.106	0.109	0.115	0.107	0.115	0.111				
20	0.110	0.133	0.127	0.134	0.132	0.123	0.116	0.118	0.121	0.127	0.120	0.127	0.123				
25	0.121	0.150	0.142	0.149	0.147	0.137	0.130	0.132	0.135	0.141	0.132	0.140	0.136				
30	0.133	0.168	0.158	0.165	0.163	0.152	0.144	0.146	0.149	0.155	0.146	0.154	0.149				
35	0.146	0.186	0.174	0.182	0.179	0.168	0.159	0.160	0.164	0.170	0.160	0.168	0.164				
40	0.160	0.205	0.191	0.199	0.196	0.184	0.175	0.176	0.179	0.185	0.175	0.183	0.178				
45	0.174	0.226	0.210	0.218	0.215	0.201	0.191	0.192	0.196	0.202	0.191	0.199	0.193				
50	0.189	0.249	0.230	0.238	0.234	0.220	0.209	0.210	0.213	0.219	0.208	0.216	0.210				
55	0.205	0.274	0.251	0.259	0.255	0.240	0.228	0.228	0.232	0.238	0.226	0.233	0.228				
60	0.222	0.301	0.274	0.283	0.277	0.261	0.249	0.248	0.252	0.257	0.245	0.252	0.247				
65	0.241	0.329	0.298	0.307	0.301	0.286	0.272	0.269	0.274	0.278	0.265	0.272	0.267				
70	0.259	0.362	0.324	0.333	0.326	0.309	0.295	0.292	0.297	0.300	0.287	0.294	0.287				
R^2	0.99996	0.99981	0.99995	0.99994	0.99996	0.99988	0.99987	0.99996	0.99994	0.99996	0.99995	0.99993	0.99994				
$\frac{\Delta_r H}{\text{kJ mol}^{-1}}$	14	17	16	15	15	15	15	15	15	14	15	14	14				
$\frac{\Delta_r S}{\text{J K}^{-1} \text{ mol}^{-1}}$	31	40	36	35	34	35	35	33	33	32	32	30	31				

As $K_{M\alpha}$ and $K_{M\beta}$ are approximately temperature independent (see previous paragraph), the terms in braces can be considered as hybrid spectra⁸ which are also temperature independent. That explains the existence of isosbestic points (pseudorank = 2) in the entire experimental temperature range for each NaNO₃ concentration.

Acknowledgement. – This work was supported by the Ministry of Science, Education and Sports of the Republic of Croatia (Project No. 119-1191342-2960).

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SAŽETAK

Utjecaj temperature na UV spektre koncentriranih vodenih otopina NaNO₃

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Proučavan je utjecaj temperature na UV apsorpcijsku vrpcu nitratnog iona u vodenim otopinama NaNO₃ ($0,2 \leq c/\text{mol dm}^{-3} \leq 4,2$). Pokusi su izvedeni u temperaturnom intervalu (15–70) °C s korakom od 5 °C. Za svaku ispitivanu otopinu uočen je batokromni pomak spektralnog maksimuma (pri ≈ 300 nm) s povišenjem temperature, kao i postojanje dobro definirane izosbestičke točke. Eksperimentalno je potvrđena reverzibilnost tih spektralnih promjena. Analiza glavnih komponenata izvedena je za svaku koncentraciju elektrolita te je utvrđeno da efektivni rang svih odgovarajućih spektralnih matrica iznosi 2. Ranije je pokazano da su u razrijeđenim vodenim otopinama prisutna dva oblika slobodnog nitratnog iona ($\alpha\text{-NO}_3^-$ and $\beta\text{-NO}_3^-$) koji se razlikuju po strukturi hidratacijske ljuske. Budući da se pri višim koncentracijama elektrolita može očekivati da oba oblika tvore ionske parove, pretpostavljeno je da se u otopini zbivaju četiri ravnotežne reakcije (interkonverzija između vrsta $\alpha\text{-NO}_3^-$ and $\beta\text{-NO}_3^-$, reakcije ionskog sparivanja tih dviju vrsta s Na⁺, te interkonverzija između ionskih parova $\{\text{Na}^+(\alpha\text{-NO}_3^-)\}$ i $\{\text{Na}^+(\beta\text{-NO}_3^-)\}$). Pokazano je, da se uočene spektralne promjene uzrokovane promjenom temperature mogu objasniti pretpostavkom o približnoj temperaturnoj neovisnosti reakcija ionskog sparivanja (odnosno odgovarajuće vrijednosti $\Delta_r H \approx 0$). U tom se slučaju spektar vodene otopine NaNO₃ može izraziti kao linearna kombinacija dvaju temperaturno neovisnih 'hibridnih' spektara. Na taj se način mogu objasniti rezultati analize glavnih komponenata, kao i postojanje izosbestičke točke u cijelom istraženom temperaturnom području.