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Enthalpies of solution of two Meisenheimer σ-adducts and tetrabutylammonium bromide in DMSO

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Abstract

Enthalpies of solution of two Meisenheimer σ-adducts of sym.-trinitrobenzene and tetrabutylammonium bromide were measured in pure dimethylsulfoxide (DMSO) at 298.15 K using a precise isoperibol calorimeter. The enthalpic coefficients of solute–solute pair-interactions and standard enthalpies of the electrolyte solution were evaluated. It has been found that the interaction between tetrabutylammonium cation and 1,1-dimethoxy-2,4,6-trinitrocyclohexa-2,5-dienide anion is enthalpically attractive, but the interaction of tetrabutylammonium cation with bromide-ion and especially with 6,8,10-trinitro-1,4-dioxaspiro[4.5]-deca-6,9-dienide anion is enthalpically repulsive.

Keywords: Meisenheimer σ-adducts; Enthalpies of solution; Solute–solute interactions

1. Introduction

Meisenheimer σ-adducts of sym.-trinitrobenzene are widely used as model compounds for investigating the mechanism of $S_{\mathrm{Ar}}N$ reactions in a solution, and also as perspective substrates for synthesising many important polyfunctional organic compounds [1–4]. The peculiarities of the anionic σ-adduct structure and a significant delocalisation of a negative charge on the complex anion are known to influence strongly the energetics of σ-adduct solvation and ion–ion interactions in a solution [5–10]. There are some studies dealing with the investigation of σ-adduct solvation and association by molecular spectroscopy [5–9] and conductometric techniques [10]. However, calorimetric studies of σ-adduct solvation and solute–solute interactions in non-aqueous solvents are nearly unavailable. The single investigation [10] dealing with the determination of the enthalpies of σ-adduct solution in dimethylsulfoxide (DMSO) indicated that the $\Delta_{\mathrm{sol}}H^m$ values strongly depended on the σ-adduct anion structure, the slopes of the curves $\Delta_{\mathrm{sol}}H^m$ versus $m^{0.5}$ being different from the limiting Debye's law.

In the present study, we report the enthalpies of solution of two σ-adducts and tetrabutylammonium bromide in DMSO and compare those with the results reported elsewhere [10]. The main purpose of this study is to compare the σ-adduct behaviour with that of simple uni-univalent electrolyte and evaluate

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the contributions of ion–ion interactions into the concentration changes of the enthalpies of solution.

2. Experimental

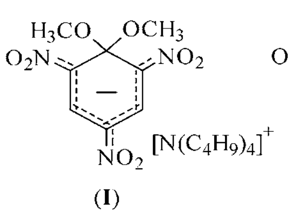
Tetrabutylammonium 1,1-dimethoxy-2,4,6-trinitrocyclohexa-2,5-dienide (σ-adduct (I)) and 6,8,10-trinitro-1,4-dioxaspiro[4.5]-deca-6,9-dienide (σ-adduct (II)) were synthesised according to the following techniques [7].

2.1. Synthesis of tetrabutylammonium 1,1-dimethoxy-2,4,6-trinitrocyclohexa-2,5-dienide

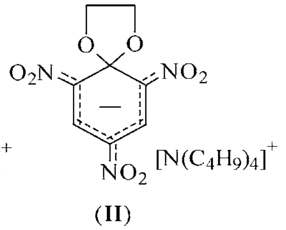
The equimolar amount of a 30% solution of tetrabutylammonium hydroxide in the water–methanol binary mixture was added to the 1-methoxy-2,4,6-trinitrobenzene solution in benzene. Cooling of the mixture up to 273 K enhanced the crystallisation. The product was washed by benzene and then reprecipitated from pure acetonitrile using tenfold surplus of diethyl ether. Then the σ-adduct (I) was dried under reduced pressure up to a constant weight and stored in a dark cool place in an exsiccator with P_2O_5.

2.2. Synthesis of tetrabutylammonium 6,8,10-trinitro-1,4-dioxaspiro[4.5]-deca-6,9-dienide

The equimolar amount of 30% aqueous solution of tetrabutylammonium hydroxide and an aqueous solution of 1-β-oxyethoxy-2,4,6-trinitrobenzene were mixed at a room temperature. Then the mixture was evaporated under reduced pressure and the product was washed by benzene and diethyl ether. The σ-adduct (II) was dried under reduced pressure at a room temperature up to a constant weight.



(I)



(II)

The structure and purity of both σ-adducts were proved by elemental analysis, IR-, UV- and NMR-spectra. The elemental analysis was carried out with Carlo Erba 1100 gas chromatographic element evaluator. The results for the σ-adduct (I) are as follows: there are found (%) C, 55.89; N, 10.82; H 8.49 ($C_{24}N_4O_8H_{44}$ requires C, 55.78; N, 10.85; O, 24.78; H 8.49), for the σ-adduct (II) the results being as follows: there are found (%) C, 56.11; N, 10.87; H 8.20 ($C_{24}N_4O_8H_{42}$ requires C, 56.00; N, 10.89; O, 24.88; H 8.23). The UV- and IR-spectra measurements were carried out using SPECORD M-40 and SPECORD M-80 spectrometers. NMR studies were performed with a Varian VXR-400 (400 MHz) apparatus. The results for the σ-adduct (I) are as follows {IR-spectrum (DMSO) ν/cm^{-1}: 1606 ($C\overset{\cdots}{-}C$), 1240 (NO_2); UV-spectrum (DMSO) $\nu/\mathrm{cm}^{-1}(\varepsilon)$: 23660 (30400), 20220 (20000); ^{1}H NMR study (acetone-d_6, δ, ppm): 8.61 (*s*, 2H, H (3), H (5)), 4.26 (*s*, 6H, H (7), H (8)); ^{13}C NMR study (DMSO-d_6, δ, ppm): 128.78 (*s*, 4C, C (2), C (3), C (5), C (6)), 117.37 (*s*, 1 C, C (4)), 59.18 (*d*, 2 C, C (7), C (8))}, for the σ-adduct (II) the results being {IR-spectrum (DMSO) ν/cm^{-1}: 1606 ($C\overset{\cdots}{-}C$), 1246 (NO_2); UV-spectrum (DMSO) ν/cm^{-1} (ε): 23900 (27700), 20340 (20800); ^{1}H NMR study (DMSO-d_6, δ, ppm): 8.48 (*s*, 2H, H (3), H (5)), 4.21 (*s*, 4H, H (7), H (8)); ^{13}C NMR study (DMSO-d_6, δ, ppm): 131.91 (*s*, 2 C, C (2), C (6)), 124.96 (*d*, 2C, C (3), C (5)), 117,76 (*s*, 1C, C (4)), 69.83 (*d*, 2 C, C (7), C (8))}.

Tetrabutylammonium bromide (Reachim, initial purity 99%) was recrystallised twice from the ethanol–ether mixture and dried under reduced pressure at 333 K up to a constant weight. DMSO was frozen at 291 K, dried by 4 Å sieves and distilled twice under reduced pressure at 330 K. IR-spectrum indicated that the water content in pure DMSO was less than 0.01 wt.%.

The measurements were carried out using a new precise thermetic “isoperibol” ampoule calorimeter fitted with 55 or 30 cm^3 interchangeable titanium calorimetric vessels. A calorimetric vessel was equipped with a calibrating heater, a titanium stirrer and a thermistor. A glass ampoule containing a solute was attached to a stirrer. An ampoule crushing against a vessel bottom initiated a dissolution process. A thermistor was connected with a precise resistance bridge and a recorder potentiometer. The enthalpy of solution was determined by a comparative method. An electrical calibration was carried out before and after each experiment.

Table 1
Experimental and standard enthalpies of solution (kJ mol^{-1}) of KCl and Bu_4NBr in water at 298.15 K

KCl		Bu_4NBr	
m[a]	$\Delta_{sol}H^m$	m	$\Delta_{sol}H^m$
0.02829	17.44	0.003570	−8.50
0.02836	17.35	0.005470	−8.47
0.02953	17.56	0.006295	−8.53
0.04231	17.45	0.006931	−8.51
0.05170	17.54	0.01024	−8.42
0.07090	17.70	0.07795	−8.33
0.07275	17.58	0.1011	−8.19
0.1006	17.55	0.1509	−7.79
0.1199	17.38	0.2021	−7.29
0.1395	17.53	0.2653	−6.67
$\Delta_{sol}H^\circ = 17.21 \pm 0.07$[b]		$\Delta_{sol}H^\circ = -8.60 \pm 0.06$[b]	
17.22[c]		−8.58[d], −8.48[e]	

[a] Moles of the solute per 1 kg of water.

[b] The uncertainties of the $\Delta_{sol}H^\circ$ values represent as twice the standard deviation of the mean values obtained.

[c] Value from [11].

[d] [13].

[e] [14].

3. Results

The calorimeter was tested by measuring the enthalpies of potassium chloride (KCl) and tetrabutylammonium bromide (Bu_4NBr) solution in water at 298.15 K. The experimental results at different solute molalities are given in Table 1. The standard enthalpies of electrolyte solution in water were calculated using the enthalpies of dilution [11,12]. The agreement between our and literature [11–14] $\Delta_{sol}H^\circ$ values in water is seen to be excellent. The overall uncertainty of the standard enthalpies of solution in water including random and systematic errors in the application [15] is estimated to be within 1%.

Both σ-adducts studied are stable and soluble enough in DMSO [7,8,10]. The main period duration of each experiment in our calorimeter did not exceed two minutes, which allowed using the Dickinson procedure for treating the experimental data [16]. The experimental enthalpies of the σ-adducts solution $\Delta_{sol}H^m$ are given in Table 2.

Table 2
Experimental enthalpies of solution (kJ mol^{-1}) of the σ-adduct (I), σ-adduct (II) and Bu_4NBr in DMSO at 298.15 K

σ-Adduct (I)		σ-Adduct (II)		Bu_4NBr	
m[a]	$\Delta_{sol}H^m$	m	$\Delta_{sol}H^m$	m	$\Delta_{sol}H^m$
0.0009978	38.02	0.000800	29.85	0.003592	20.25
0.001488	37.92	0.001476	30.83	0.006866	20.18
0.001948	37.87	0.001953	31.05	0.02180	20.30
0.002380	37.79	0.002425	31.60	0.03312	20.31
0.003113	37.81	0.003847	32.17	0.05231	20.33
0.004143	37.42	0.005991	32.87	0.07563	20.41
0.01107	36.77	0.009756	32.71	0.1065	20.47
0.01943	36.52	0.01493	32.78	0.1304	20.55

[a] Moles of the solute per 1 kg of DMSO.

4. Discussion

The results obtained are represented in Fig. 1. The experimental curves $\Delta_{sol}H^m$ versus $m^{0.5}$ are seen to deviate from the limiting Debye's slope, the deviation increasing in the range Bu_4NBr < σ-adduct (I) < σ-adduct (II). It should be noted that the deviation for the solutes with a common cation has different signs—the σ-adduct (II) and tetrabutylammonium bromide show a positive deviation, but the σ-adduct (I) indicates a negative one. Therefore, it is important to evaluate the contributions of ion–ion interactions into the concentration changes of the $\Delta_{sol}H^m$ values. The procedure proposed by Levine and Wood [12] taking into account the Debye's limiting law and ion–ion pair-interactions appears to be reasonable for treating the experimental data:

$$\Delta_{sol}H^m = \Delta_{sol}H^\circ + a_H m^{0.5} + \{CC + AA + CA\}m + \{CC + AA - CA\}2A_\gamma m^{1.5} + \cdots \quad (1)$$

where $\Delta_{sol}H^\circ$ is the standard enthalpy of solution, the $\{CC + AA + CA\}$ and $\{CC + AA - CA\}$ are the coefficients reflecting the contributions of cation–cation, anion–anion and cation–anion pair-interactions into the concentration changes of the $\Delta_{sol}H^m$ values; A_γ is the parameter of the Debye–Hückel equation for the activity coefficient and a_H is the Debye's limiting slope for the apparent molal enthalpy [12]. The A_γ and a_H parameters can be defined for uni-univalent electrolytes according to the well-known relationships [17]:

$$A_\gamma = \sqrt{\frac{2\pi N A^{e^6} \rho}{1000(\varepsilon k T)^3}} \quad (2)$$

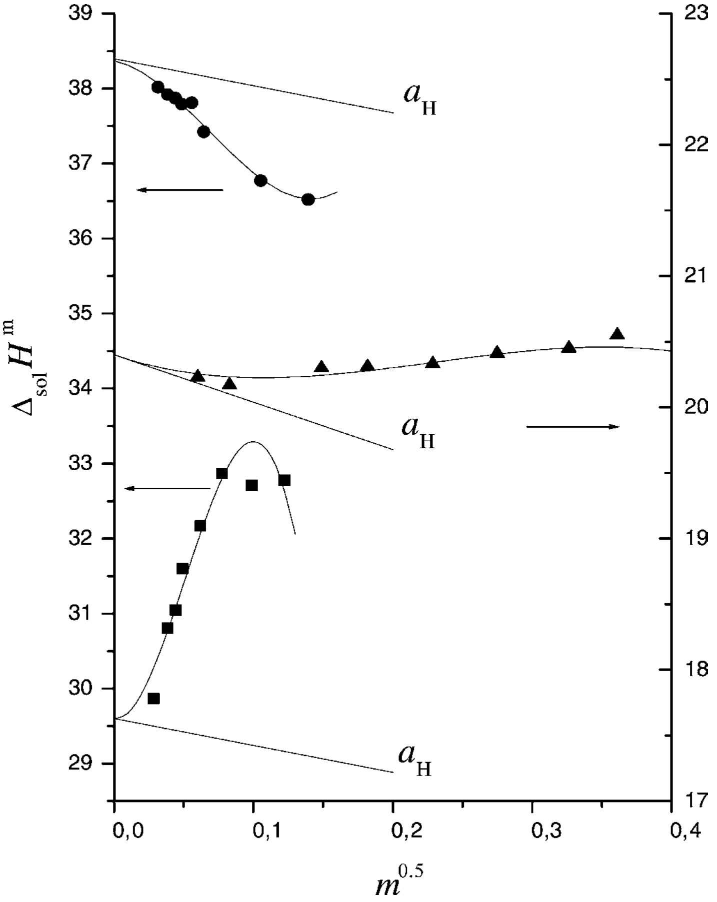


Fig. 1. Experimental (points) and calculated according to Eq. (1) (lines) enthalpies of solution (kJ mol^{-1}) of tetrabutylammonium 1,1-dimethoxy-2,4,6-trinitrociclohexa-2,5-dienide (●), 6,8,10-trinitro-1,4-dioxaspiro[4.5]-deca-6,9-dienide (■) (left-hand scale) and tetrabutylammonium bromide (▲) (right-hand scale) in DMSO at 298.15 K. a_H, the limiting Debye's law for the apparent molal enthalpy.

$$a_H = -2RT^2 A_\gamma \left(\frac{1}{T} + \frac{1}{\varepsilon}\frac{\partial \varepsilon}{\partial T} - \frac{1}{3\rho}\frac{\partial \rho}{\partial T}\right) \qquad (3)$$

DMSO density, relative permittivity and their temperature derivatives at 298.15 K were obtained from the data reported elsewhere [18,19]. These values with the A_γ and a_H parameters are listed in the note to Table 3.

The enthalpies of solution at infinite dilution $\Delta_{sol}H^\circ$ and the {CC + AA + CA} and {CC + AA − CA} coefficients were recovered from the experimental $\Delta_{sol}H^m$ data by fitting them to Eq. (1) and are given in Table 3. The comparison of the calculated and experimental $\Delta_{sol}H^m$ values is represented in the given figure. It can be seen that Eq. (1) describes the experimental data successfully enough. Table 3 shows that the $\Delta_{sol}H^\circ$ values for both σ-adducts differ from those reported earlier [10]. This disagreement appears to arise from the peculiarities of calorimetric measurements [10] where the $\Delta_{sol}H^m$ values have been determined using a shaking MCDP-2 microcalorimeter (USSR) with 15 cm^3 teflon calorimetric vessel. This type of the apparatus in our opinion is scarcely applicable for such measurements because of low hermeticity and a very prolonged main period of the dissolution experiment for slightly soluble substances. As for tetrabutylammonium bromide, our $\Delta_{sol}H^\circ$ value is seen to be in a good agreement with those reported by Krishnan and Friedman [20] and Heuvelsland et al. [21].

Let us compare the {CC + AA + CA} and {CC + AA − CA} values obtained. It is obvious that at

Table 3
Standard enthalpies of electrolytes solution (kJ mol^{-1}) and solute–solute pair-interaction coefficients (kJ kg mol^{-2}) obtained according to Eq. (1)[a]

Solute	$\Delta_{sol}H^{\circ}$	{CC + AA + CA}	{CC + AA − CA}	R	S
σ-Adduct (I)	38.36 ± 0.07, 22.47 ± 0.3[b]	−225 ± 38	206 ± 49	0.993	0.08
σ-Adduct (II)	29.62 ± 0.27, 33.47 ± 0.3[b]	1148 ± 191	−1391 ± 277	0.965	0.33
Bu_4NBr	20.40 ± 0.05, 20.71[c] ± 20.83[d]	22 ± 3	−6 ± 1	0.944	0.05

Note: The parameters of DMSO [18,19] are as follows: $\varepsilon = 46.45$; $\rho = 1.09566\,\text{g cm}^{-3}$; $\partial\epsilon/\partial T = 0.128\,\text{K}^{-1}$; $\partial\rho/\partial T\ 10^3 = 1.01\,\text{g cm}^{-3}\,\text{K}^{-1}$; $A_\gamma = 2.70\ \text{kg}^{0.5}\,\text{mol}^{-0.5}$; $a_H = -3.61\,\text{kJ kg}^{0.5}\,\text{mol}^{-1.5}$.

[a] The uncertainties of the $\Delta_{sol}H^{\circ}$, {CC + AA + CA} and {CC + AA − CA} values represent as the standard deviation of the mean values; *S*, the standard deviation of the fit (kJ mol^{-1}).

[b] Values from [10].

[c] [20].

[d] [21].

low solute concentrations (where the *m* term predominates) the deviation from the limiting Debye's law is the sum of the identically and oppositely charged interactions because of the $m^{1.5}$ term gives sufficiently small contribution. As the concentration increases the last term of Eq. (1) becomes more important, the effect of cation–anion interactions is reduced and the contributions cation–cation and anion–anion interactions are increased [12]. It is obvious that in the systems studied the *m* term predominates and the deviation from the Debye's law is the sum of the identically and oppositely charged interactions. The cation–cation pair-interaction is seen to be identical in the systems studied and then the solutes behaviour is defined by cation–anion and anion–anion interactions. The analysis of the difference between the {CC+AA+CA} and {CC+AA−CA} coefficients allows to draw a conclusion that the deviation from the limiting Debye's slope in the systems studied results from predominantly cation–anion pair-interactions. The interaction between tetrabutylammonium cation and 1,1-dimethoxy-2,4,6-trinitrociclo-hexa-2,5-dienide anion is enthalpically attractive, which results in a slightly negative deviation from the limiting Debye's slope. On the other hand, the interaction of Bu_4N^+ cation with 6,8,10-trinitro-1,4-dioxaspiro[4.5]-deca-6,9-dienide anion is strongly enthalpically repulsive that causes a large positive deviation (see Figure). It is interesting to note that the enthalpies of Bu_4NBr solution in DMSO are almost independent from the solute molality. This result differs from that observed in pure water where the $\Delta_{sol}H^m$ values depend significantly on the Bu_4NBr molality (see Table 1) due to hydrophobic effects occurring in aqueous solutions of non-polar particles.

It is known that σ-adducts of sym.-trinitrobenzene show a tendency to association in non-aqueous solvents [4–9]. The association constants (K_a) for the σ-adducts (I) and (II) in DMSO at 298.15 K obtained from the conductometric data are 500 and 250 cm^3 mol^{-1}, respectively [10]. At the same time, IR-spectra studies [8,9] indicated that the σ-adducts (I) and (II) were unlikely to form contact cation–anion pairs in DMSO. Thus, sufficiently large K_a values observed result from the influence of the solvent separated configurations. It seems surprising that for the solute with the smaller association constant the larger deviation is observed and vice versa (see Figure). Since the association enthalpies are defined from the temperature derivatives of the K_a values, the conductometric studies of the σ-adduct solution at different temperatures appear to be useful to understand the theoretical point of view of the results obtained.

5. Conclusions

The calorimetric study of Meisenheimer σ-adducts of sym.-trinitrobenzene solution indicates a strong dependence of the $\Delta_{sol}H^m$ values from the solute molality in comparison with a simple uni-univalent electrolyte with a common cation. The results obtained significantly indicate that the σ-adduct behaviour in a diluted solution is defined to a great extent by cation–anion interactions, their energetics greatly depending on anion structure.

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