

# SOLUBILITIES AND THERMODYNAMICS OF TRANSFER OF *o*- AND *m*-NITROANILINES IN AQUEOUS 2-METHOXYETHANOL MIXTURES AND THE SOLVENT EFFECT ON THE DISSOCIATION OF THE PROTONATED BASE

A.O. Barakat, A.A. El-Harakany, H. Sadek and M.F. Omar

Department of Chemistry, Faculty of Science, Alexandria University,  
PO Box 426, 21321 Alexandria, Egypt

## ABSTRACT

The solubilities of *o*-ortho and *meta*-substituted nitroanilines were determined at five different temperatures to obtain the thermodynamic parameters of transfer of the bases from water to the mixed solvent systems. The results are interpreted in terms of the structural changes occurring in the solvent mixtures with the change in solvent composition. The solvent effect has been discussed in terms of the free energies of transfer  $\Delta G_t^\circ(i)$  from water to the aqueous 2-methoxyethanol solvents, of the uncharged base (B) evaluated from measured solubilities, of the hydrochloride of the base (B.HCl) computed from the corresponding values for HCl, and also of the individual ions assessed from the previous knowledge of  $\Delta G_t^\circ(\text{Cl}^-)$ .

*Keywords: Solubility, o-nitroaniline, m-nitroaniline, Thermodynamic transfer parameters, 2 methoxyethanol.*

## INTRODUCTION

It is now a well recognized fact that the dissociation of weak acids and bases in mixed solvent media is a function not only of electrostatic effects related to the charge type of the acid-base pair but is also influenced profoundly by specific solvation of the acid, its conjugate base, and the proton [1,2]. The relative effectiveness of the two components of the solvent mixture in stabilizing these individual species can often be revealed by emf, pH, or spectrophotometric measurements in combination with solubility measurements [3-9].

Recently [10], the dissociation constants of *ortho*- and *meta*-nitroanilinium ions in water-2-methoxyethanol solvent mixtures at 25°C have been determined by spectrophotometric measurements. The solvent effects on the dissociation behavior of these acids,  $\Delta G_t^\circ[\text{BH}^+-\text{B}]_{\text{sys}} = 2.303[p(\text{K})_{\text{BH}^+} - p(\text{K})_{\text{BH}^+}]$ , in these media result in the characteristic minima with the solvent composition. For a better understanding of the solvent effect on the dissociation behavior of these two acids, the probable contribution of the uncharged species (B) taking part

in the acid-base reaction, was determined from measurements of the solubilities (S) of the amines in water-2-methoxyethanol (MCS) solvents containing from zero to 100% MCS. Further, the standard thermodynamic functions of transfer for the dissolution process of *ortho*- and *meta*-nitroaniline in the various mixtures of water-MCS have been derived from the variation of their solubilities with temperature.

## EXPERIMENTAL

The solubilities of *ortho*- and *meta*-NA were determined by a method similar to that of Barakat and El-Harakany [5]. Three aliquots from each saturated solution were withdrawn with a capillary pipette, carefully drained into a 100 mL ground joint neck Erlenmeyer flasks, stoppered, and weighed to the nearest 0.01 mg. The saturated solutions were appropriately diluted with water in order to restrict absorbance values within the range 0.1-0.9, and analysed by measuring the optical absorbance using

a Pye Unicam Spectrophotometer 1800B. The molal extinction coefficients of *o*- and *m*-nitroanilines were found to be  $3.920 \times 10^3$  and  $1.291 \times 10^3$ , respectively, from the standard calibration curve using ten standard solutions.

2-methoxyethanol at five experimental temperatures 20, 25, 30, 35, and 40°C are collected in Table (1), together with their relative deviations. The values in water at 25°C are found to be  $6.9 \times 10^{-3}$  mol Kg<sup>-1</sup> (*o*-NA) and  $9.5 \times 10^{-3}$  mol Kg<sup>-1</sup> (*p*-NA), which agrees fairly well with the literature values of  $6.8 \times 10^{-3}$  mol Kg<sup>-1</sup> [e.g. 4, 11] and  $9.1 \times 10^{-3}$  mol Kg<sup>-1</sup> [12], respectively.

RESULTS AND DISCUSSION

The solubilities of *o*- and *m*-nitroanilines (mole fraction scale) in pure water and aqueous mixtures of

Table 1. Solubilities of *o*- and *m*-nitroanilines in water-2-methoxyethanol mixtures from 20 to 40°C\*.

Wt.% MCS	20°C		25°C		30°C		35°C		40°C	
	10 <sup>4</sup> S	r.d.#	10 <sup>4</sup> S	r.d.	10 <sup>4</sup> S	r.d.	10 <sup>4</sup> S	r.d.	10 <sup>4</sup> S	r.d.
<i>m</i> -nitroaniline										
0	1.443	0.07	1.722	0.17	2.193	0.83	2.635	0.46	3.259	0.25
10	2.309	0.37	2.934	0.21	3.619	0.15	4.595	0.54	5.906	0.63
30	8.579	0.01	12.42	0.86	15.00	0.33	19.26	0.90	25.00	1.24
50	67.66	0.67	88.25	0.36	129.0	0.01	156.5	0.32	210.0	1.59
70	498.0	0.13	589.0	0.49	794.0	0.50	868.0	0.76	1077	0.50
100	2132	0.11	2236	0.16	2356	0.83	2603	0.52	2725	0.20
<i>o</i> -nitroaniline										
0	1.010	0.01	1.249	0.15	1.489	0.08	1.872	1.72	2.266	0.26
10	1.491	0.91	1.878	0.07	2.305	0.07	2.958	0.36	3.652	0.94
30	4.495	0.94	5.902	0.18	7.526	0.59	9.841	0.30	12.86	1.00
50	28.42	0.60	36.39	0.57	44.31	0.65	58.29	0.62	73.32	0.99
70	192.7	0.05	220.8	0.24	253.0	0.26	299.2	0.06	342.0	0.10
100	123.0	0.16	1246	0.25	1341	1.81	1448	0.02	1486	0.15

\*Mole fraction scale  
#Relative deviation (per cent)

The variation of the solubility with the temperature for each solvent composition was expressed by fitting log S at the different temperatures by the method of least square to Equation (1) of the form suggested by Kundu *et al.* [13],

$$\log S = A + B/T + C \ln T \quad (1)$$

where T is the Kelvin temperature. The standard thermodynamic quantities ΔG°, ΔH°, and ΔS° for the dissolution process were derived from the Equations (2-4)

$$\Delta G^\circ = -2.303 RT \log S = -2.303R[A_1 + A_2 + A_3 T^2] \quad (2)$$

$$\Delta S^\circ = -d\Delta G^\circ/dT = 2.303R[A_1 + 2A_3 T] \quad (3)$$

$$\Delta H^\circ = \Delta G^\circ + \Delta S^\circ = 2.303R[-A_2 + A_3 T^2] \quad (4)$$

where  $A$ ,  $A_1$  and  $A_2$  are constants.

The standard Gibbs energies of transfer of the uncharged bases (B), the nitroanilines, from water to the mixed solvents at 25°C were computed by using the method described previously [1, 2] using the relation,

$$\Delta G^\circ_t(B) = \Delta_s G^\circ(B) - \Delta_w G^\circ(B) \quad (5)$$

$$= 2.303RT \log(N_w/N_s) \quad (6)$$

where  $N_w$  and  $N_s$  are the solubilities of the base in water and respective solvents (SH) in mole fraction scale. The corresponding standard entropy of transfer,  $\Delta S^\circ_t(B)$ , and enthalpy of transfer,  $\Delta H^\circ_t(B)$ , were computed from equations (6) and (7), respectively,

$$\Delta S^\circ_t(B) = \Delta_s S^\circ(B) - \Delta_w S^\circ(B) \quad (7)$$

$$\Delta H^\circ_t(B) = \Delta_s H^\circ(B) - \Delta_w H^\circ(B) \quad (8)$$

The values  $\Delta G^\circ_t$ ,  $\Delta S^\circ_t$ , and  $\Delta H^\circ_t$  at 25°C are listed in Table (2).

#### Thermodynamic functions of transfer.

The values of  $\Delta G^\circ_t(B)$  for the nitroanilines in MCS-H<sub>2</sub>O solvent system are found to be negative, the magnitudes increasing with increasing proportion of the non-aqueous component in the solvent mixtures. The benzene ring being hydrophobic, nitroanilines should have a greater affinity towards the organic solvents, resulting in increasingly negative contributions to  $\Delta G^\circ_t(B)$  values. Solvation will also occur through hydrogen bond formation in which the NH<sub>2</sub> as well as the NO<sub>2</sub> group will be involved, and these factors should make their independent contributions to the overall values of  $\Delta G^\circ_t(B)$ . Owing to the inductive effect of the methyl group in 2-methoxyethanol, the negative charge density on the oxygen atom ( $^m\delta_-$ ) is presumably somewhat

greater than the corresponding quantity in water ( $^w\delta_-$ ), so that the protonic character of the hydrogen atom of the hydroxygroup in 2-methoxyethanol ( $^m\delta_+$ ) is weaker than that in water ( $^w\delta_+$ ) [14]. The increasingly negative values for  $\Delta G^\circ_t(B)$  (Table 2), therefore, may primarily be attributed to the larger stabilization of the base due to the dispersion interaction of the benzene nucleus of the nitroaniline with the organic component of the solvent mixture.

The variations of the values of  $\Delta G^\circ_t(B)$  for *o*-NA and *m*-NA are compared in Figure (1) with the corresponding variation for *p*-NA in aqueous 2-methoxyethanol solvents [5]. The  $\Delta G^\circ_t(B)$  values for both *o*-NA and *p*-NA are found to be almost the same and show less negative values as compared with those of *m*-NA. This indicates that the nature of interaction of the nitroanilines with the solvent dipoles are somewhat different. The *o*- or *p*-nitro group can enter into resonance with the unshared pair of the N atom of the amino group, which is not possible for a *m*-nitro group; therefore, the charge densities on the atoms of the substituent groups are not similar in the *o*- or *p*-nitroaniline as compared to *m*-nitroaniline. Moreover, the steric effect in *o*-NA is expected to play an important role in the extent of interaction of the two substituent groups with the solvent dipoles. These differences are reflected in the relative positions of the  $\Delta G^\circ_t(B)$  curves.

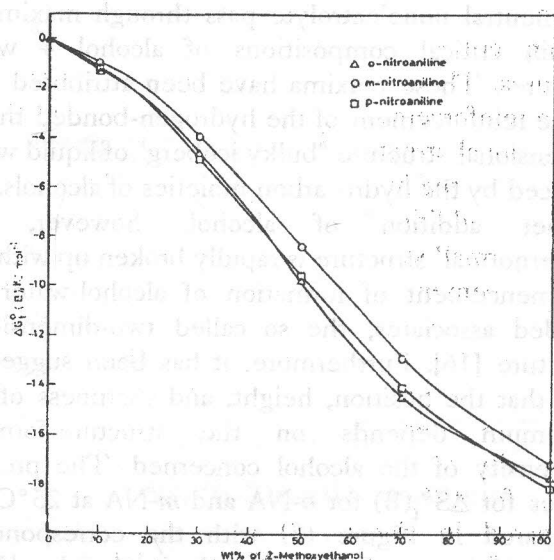


Figure 1. Variation of  $\Delta G^\circ_t(B)$  of *o*-NA, *m*-NA, and *p*-NA as a function of concentration of 2-methoxyethanol at 25°C.

**Table 2.** Thermodynamic functions of transfer of *o*- and *m*-nitroaniline from water to aqueous 2-methoxyethanol solvents at 25°C\*.

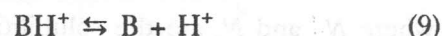
Mol% MCS	wt% MCS	$\Delta G^\circ_t[B]/kJ\ mol^{-1}$		$\Delta S^\circ_t[B]/J\ mol^{-1}$		$\Delta H^\circ_t[B]/kJ\ mol^{-1}$	
		<i>o</i> -NA	<i>m</i> -NA	<i>o</i> -NA	<i>m</i> -NA	<i>o</i> -NA	<i>m</i> -NA
2.56	10	-1.25	-1.02	18.12	14.84	4.16	3.39
9.20	30	-4.63	-3.85	48.85	43.21	9.94	9.01
19.10	50	-9.80	-8.35	75.63	45.49	12.76	5.19
35.60	70	-14.49	-12.86	42.26	13.94	-1.90	-8.72
100.00	100	-17.74	-17.19	-12.82	-18.11	-21.56	-22.61

The results presented in Table (2) for the change of entropy and enthalpy of transfer, provide significant evidence that these two functions follow a parallel path; whereby they pass through a maximum at a composition of about 40 % MSC, beyond which they assume less positive decrease rapidly upon further addition of the solvent content.

In earlier studies [13,15], the thermodynamic quantities, specifically the entropy, of transfer of quite a number of inert non-electrolytes have been used to reveal preferential solvation and structural information in aqua-alcoholic mixtures. It has been observed by various workers [16,17] that entropies of transfer of various electrolytes, polar nonelectrolytes, and neutral nonelectrolyte pass through maxima at certain critical compositions of alcohol + water mixtures. These maxima have been attributed [15] to the reinforcement of the hydrogen-bonded three-dimensional structure "bulky iceberg" of liquid water induced by the hydrocarbon moieties of alcohols. On further addition of alcohol, however, the "supernormal" structure is rapidly broken up with the commencement of formation of alcohol-water H-bonded associates, the so called two-dimensional structure [16]. Furthermore, it has been suggested [13] that the position, height, and sharpness of the maximum depends on the structure-forming propensity of the alcohol concerned. The present values for  $\Delta S^\circ_t(B)$  for *o*-NA and *m*-NA at 25°C are compared in Figure (2) with the corresponding values of the transfer of *p*-NA obtained earlier [5]. It is apparent that the position of the maximum shifts slightly to higher solvent content according to the following order:

*o*-nitroaniline > *m*-nitroaniline > *p*-nitroaniline

*Solvent effects.* The solvent effect on the dissociation of  $BH^+$  ion,



$\Delta G^\circ_t[BH^+-B]_{sys}$ , has been calculated earlier [10] using Eq. (10),

$$\Delta G^\circ_t[BH^+-B]_{sys} = \Delta G^\circ - {}_w\Delta G^\circ = 2.303$$

$$RT[p({}_sK)_N - p({}_wK)_N] \quad (10)$$

which can be expressed [1, 2, 5, 6] in the form of,

$$\Delta G^\circ_t[BH^+-B]_{sys} = \Delta G^\circ_t(HCl) + \Delta G^\circ_t(B) - \Delta G^\circ_t(B.HCl) \quad (11)$$

$$= \Delta G^\circ_t(H^+) + \Delta G^\circ_t(B) - \Delta G^\circ_t(BH^+) \quad (12)$$

where  $\Delta G^\circ_t(i)$  is the Gibbs energy change accompanying the transfer of one mole of species *i* from the standard state in water to the standard state in the solvent concerned.

The standard free energy of the transfer of the hydrochlorides,  $\Delta G^\circ_t(B.HCl)$  from water to the mixed solvents at 25°C have been evaluated from equation (11), with the values of  $\Delta G^\circ_t[BH^+-B]_{sys}$  obtained earlier [10] and the values of  $\Delta G^\circ_t(HCl)$  at 25°C being obtained from the literature [18]. The values of  $\Delta G^\circ_t(HCl)$  and  $\Delta G^\circ_t[BH^+-B]$  for the two nitroanilines are summarized in Table 3 together with the calculated values of  $\Delta G^\circ_t(B.HCl)$ . Table 3 shows that there is similarity in the trend of

$\Delta G^\circ_t(B.HCl)$  values for both nitroanilines. Thus, the values pass through a maximum at a composition of 10 wt. % MCS beyond which they decrease with increasing proportion of MCS in the mixture. A characteristic difference, however, is the large decreasing values of  $\Delta G^\circ_t(B.HCl)$  (Table 3) for *o*- $NAH^+$ , which indicates preferential stabilization of the latter with increasing solvent proportions as compared to *m*- $NAH^+$ .

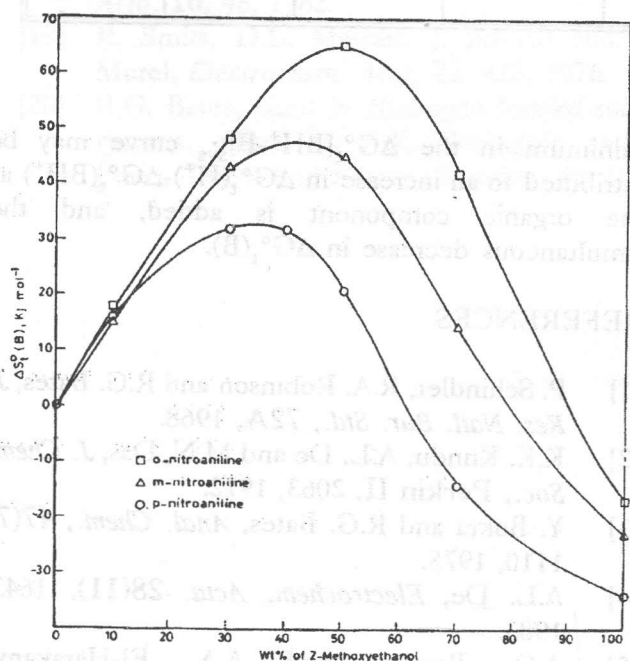


Figure 2. Variation of  $\Delta S^\circ_t(B)$  of *o*-NA, *m*-NA and *p*-NA as a function of concentration of 2-methoxyethanol at 25°C.

For a better understanding of the nature of ion-solvent interactions, splitting of the free energy of transfer into its ionic contributions is essential. The values of  $\Delta G^\circ_t(BH_2^+)$  and  $\Delta G^\circ_t(H^+)$  in equation (12) have been evaluated by utilizing the values of  $\Delta G^\circ_t(Cl^-)$  obtained from the literature [19] similarly as in the case of  $\Delta G^\circ_t(BH^+)$  for Tris and *p*- $NAH^+$  [5]. These values are also listed in Table 3.

The standard energies of transfer,  $\Delta G^\circ_t(i)$  of the individual species participating in the acid-base process (Eq. 9 and 12) are represented in Figures (3) and (4), for the dissociation of *o*- $NAH^+$  and *m*- $NAH^+$ , respectively. The plots in the latter Figures

show the preferential stabilization of the three individual species B,  $BH^+$ , and  $H^+$  by 2-methoxyethanol over water. A characteristic difference, however, between the two nitroanilines is that in the case of *m*-NA, the  $\Delta G^\circ_t(BH^+)$  curve lies above the curve for  $\Delta G^\circ_t(B)$  while the reverse is true in the case of *o*-NA. Nevertheless,  $\Delta G^\circ_t(H^+ - BH^+)$  values are positive in both cases. It is evident that similar to the interaction behavior of the two bases, the interactions of the two  $BH^+$  ions are also different. However, in this case the protonated form of *o*-nitroaniline cannot show resonating structure (lone pair of  $:NH_2$  group becomes tagged with  $H^+$  of  $NH_3^+$  group). Thus, unlike the free bases, the nature of interaction of the groups in both nitroanilinium ions would be the same. Therefore, the differences in the relative positions in the  $\Delta G^\circ_t(BH^+)$  curves indicates that steric factors are presumably the largest single factor causing an increased affinity of *o*- $NAH^+$  (as compared to *m*- $NAH^+$ ) towards the organic component-rich solvent, and outweighs any specific solvation effects.

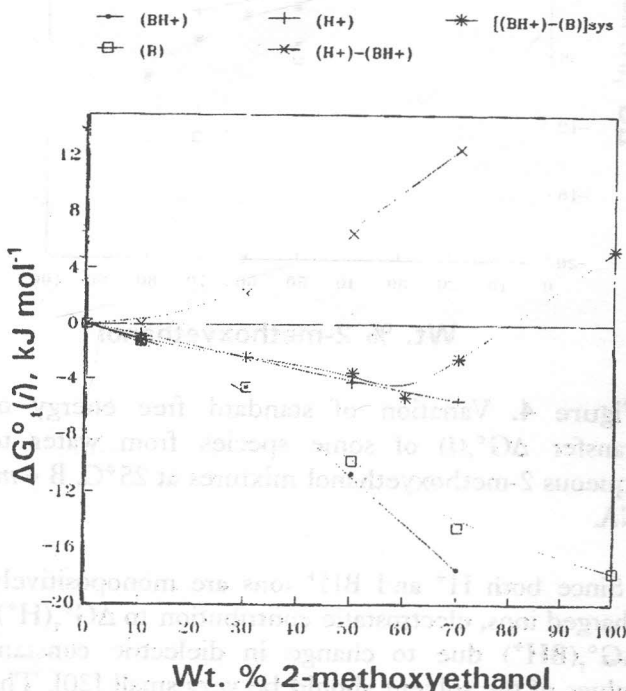


Figure 3. Variation of standard free energy of transfer  $\Delta G^\circ_t(i)$  of some species from water to aqueous 2-methoxyethanol mixtures at 25°C. B = *o*-NA.

Table 3. Standard free energies of transfer,  $\Delta G_t^\circ(i)$ , in the dissociation process of *o*-NAH<sup>+</sup> and *m*-NAH<sup>+</sup> in water-2-methoxyethanol solvent mixtures at 25°C\*.

Wt. % MCS	$\Delta G_t^\circ(\text{BH}^+-\text{B})_{\text{sys}}$		$\Delta G_t^\circ(\text{HCl})$	$\Delta G_t^\circ(\text{B.HCl})$		$\Delta G_t^\circ(\text{H}^+)$	$\Delta G_t^\circ(\text{BH}^+)$	
	<i>o</i> -NAH <sup>+</sup>	<i>m</i> -NAM <sup>+</sup>		<i>o</i> -NAH <sup>+</sup>	<i>m</i> -NAH <sup>+</sup>		<i>o</i> -NAH <sup>+</sup>	<i>m</i> -NAH <sup>+</sup>
10	-1.22	-1.29	0.25	0.231	0.52	-0.74	-0.76	-0.47
30	-2.40	-2.69	0.69	-1.44	-0.39	-2.36	-4.59	-3.52
50	-3.24	-5.17	1.65	-4.82	-1.53	-4.23	-10.70	-7.41
70	-2.48	-7.25	4.30	-7.72	-1.31	-5.51	-17.50	-11.10
100	5.33	-0.66						

\* In kJ mol<sup>-1</sup>, mole fraction scale

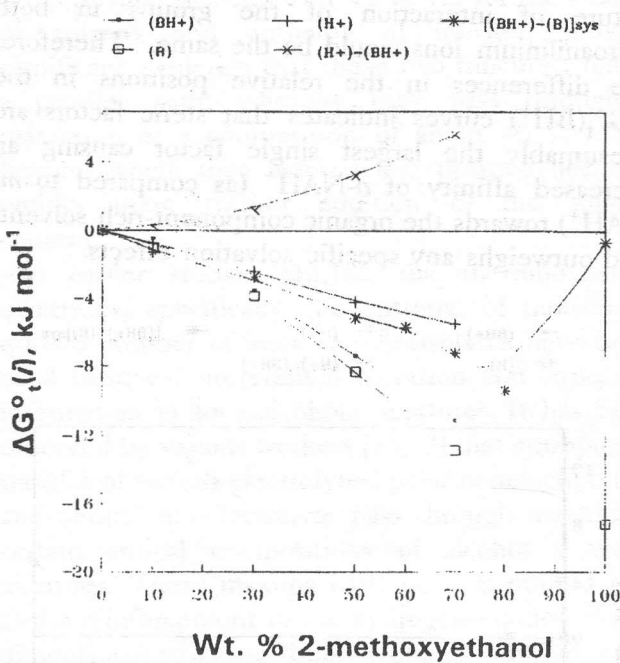


Figure 4. Variation of standard free energy of transfer  $\Delta G_t^\circ(i)$  of some species from water to aqueous 2-methoxyethanol mixtures at 25°C. B = *m*-NA.

Since both H<sup>+</sup> and BH<sup>+</sup> ions are monovalent cations, electrostatic contribution to  $\Delta G_t^\circ(\text{H}^+)-\Delta G_t^\circ(\text{BH}^+)$  due to change in dielectric constant values of the solvent should be very small [20]. The more positive values of  $\Delta G_t^\circ(\text{H}^+)$  as compared to  $\Delta G_t^\circ(\text{BH}^+)$  values (see Table 3; Figures 3 and 4), therefore, reflects the dispersion interaction of the benzene ring of BH<sup>+</sup> ion with organic component of the solvent which is absent for H<sup>+</sup> [5]. The

minimum in the  $\Delta G_t^\circ[\text{BH}^+-\text{B}]_{\text{sys}}$  curve may be attributed to an increase in  $\Delta G_t^\circ(\text{H}^+)-\Delta G_t^\circ(\text{BH}^+)$  as the organic component is added, and the simultaneous decrease in  $\Delta G_t^\circ(\text{B})$ .

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