

# Chemical Oceanography of the Arabian Sea: Part II-Equilibrium of Inorganic Nitrogen System

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The concept  $pE$ , expressed as a dimensionless quantity to study the redox potential of a system at equilibrium, is applied to study the chemistry of the system  $\text{NO}_3^- - \text{NO}_2^- - \text{NH}_4^+$  in the northern Arabian Sea. Values observed are found to be close to the equilibrium values calculated from theoretical relations and are nearer to the more recent concept of the normal value for sea water. It is inferred that the system approaches equilibrium conditions in the deeper waters of the oceans along with the  $\text{O}_2 - \text{H}_2\text{O}_2$  couple.

SILLÉN<sup>1</sup>, in his studies on equilibrium conditions in a model ocean, applied the concept  $pE$  for the first time in marine chemistry.  $pE$  was expressed as a dimensionless quantity to study the redox potential of a system at equilibrium, where at 25°C,  $pE = -\log \{e^-\} = FE_h/2.3 RT = E_h/0.059$ . Using the  $\text{O}_2 - \text{H}^+ - \text{H}_2\text{O}$  system at  $pH$  8.1, the  $pE$  of sea water was calculated as  $12.5 \pm 0.2$  (ref. 2). Wide deviations from these were observed while calculating the  $pE$  values basing on  $\text{NO}_3^- - \text{NO}_2^- - \text{NH}_4^+$  system<sup>3</sup>. On the basis of the  $\text{O}_2 - \text{H}_2\text{O}_2$  couple, Breck<sup>4</sup> obtained a  $pE$  value of around +8.5 for normal sea water at  $pH$  8.1 and at 25°C.

The above studies were from laboratory experiments under idealized conditions or equilibrium calculations from theoretical models. Perhaps the only attempt so far to study  $pE$  values from measurements in marine areas is by Sen Gupta<sup>3</sup> who attempted to test the equilibrium conditions of the inorganic nitrogen system in semi-enclosed basins periodically or permanently anoxic at depths.

In the present paper, the equilibrium conditions of inorganic nitrogen compounds from measured values of  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and  $\text{NH}_4^+$  in the Arabian Sea applying the parameter  $pE$  were examined. The data were collected during the Arabian Sea cruises of INS *Darshak* in 1973-74. Comparisons have been made with some relevant data collected by RV *Meteor* of West Germany in 1964-65 during the International Indian Ocean Expedition.

Basing calculations on the stability constants of Sillén and Martell<sup>5</sup>, the following relations have been deduced. The system  $\text{NO}_3^- - \text{NO}_2^- - \text{NH}_4^+$  has been separated into 3 redox pairs  $\text{NO}_2^-/\text{NO}_3^-$ ,  $\text{NH}_4^+/\text{NO}_3^-$ , and  $\text{NH}_4^+/\text{NO}_2^-$ . Relations for all of them have been calculated individually, which are as follows

$$2pE = 28.4 - 2pH - \log\{\text{NO}_2^-/\text{NO}_3^-\} \quad \dots(1)$$

$$8pE = 119.2 - 10pH - \log\{\text{NH}_4^+/\text{NO}_3^-\} \quad \dots(2)$$

$$6pE = 90.8 - 8pH - \log\{\text{NH}_4^+/\text{NO}_2^-\} \quad \dots(3)$$

## Methods

Samples were collected from standard hydrographic casts from the stations in the block area

shown in Fig. 1 and were analysed on board for nitrate, nitrite, ammonia and  $pH$  using the following methods:

Nitrate was analysed by the cadmium-amalgam reduction method of Morris and Riley<sup>6</sup> buffering the samples with ammonium chloride<sup>7</sup>. Nitrite was analysed by the method of Bendschneider and Robinson<sup>8</sup>. Turbidity blanks were run by adding 0.5 ml sulphanilamide solution/25 ml sample wherever found necessary. Ammonia was estimated during the *Meteor* cruise by the hypobromite-Bordeaux B method of Koroleff<sup>9</sup>. During the *Darshak* cruises this was estimated by the indophenol

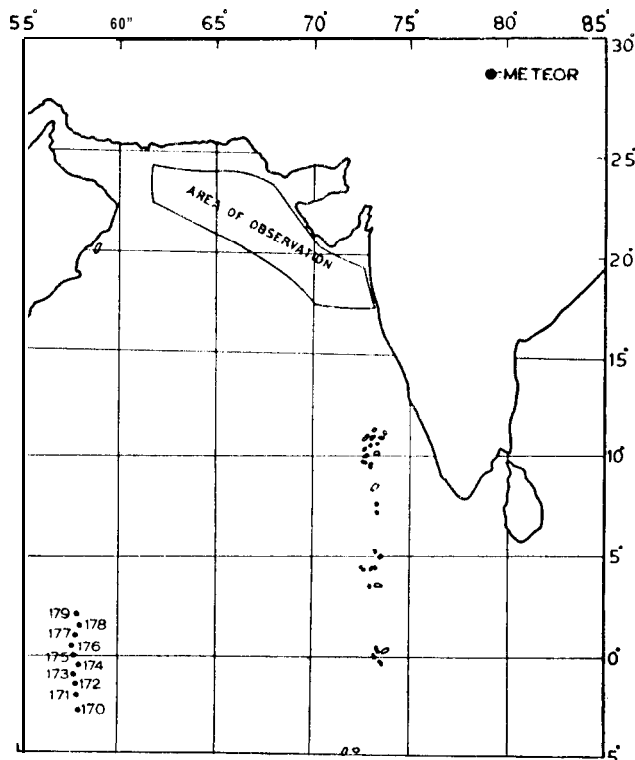


Fig. 1 -Area of observation [stations 170 to 179 are from *Meteor* cruise in 1964-65]

blue method buffering the samples with a citrate solution to avoid precipitation<sup>10</sup>. *pH* values were converted to *in situ* values after correcting for temperature and pressure effects.

Results and Discussion

**Physico-chemical** — Hydrochemically the Arabian Sea presents a very interesting picture. At an intermediate depth, between 100 and 500 m, the oxygen concentration decreases to about 0.1 ml/litre. At this level of oxygen concentration  $\text{NO}_3^-$  should be converted to  $\text{N}_2$  (g). But the process does not reach its completion since there is quite often a maximum of  $\text{NO}_2^-$  in this layer. As this layer extends over almost the whole of the Arabian Sea it can be called a suboxic layer which has been defined as a habitually oxygen deficient layer characterized by the appearance of  $\text{NO}_2^-$  just below the mixed surface layer<sup>4</sup>. Below this depth, conditions gradually transform to oxic and in deep and bottom waters, the concentration of oxygen reaches almost the surface values. The data are examined in the light of these hydrochemical characteristics. Due to photosynthetic processes the upper layers of natural water bodies are never in equilibrium with respect to any chemical system. We have, therefore, excluded the values above 100 m from calculations.

Fig. 2 presents the average of all *pE* values calculated for the 3 redox pairs in the northern

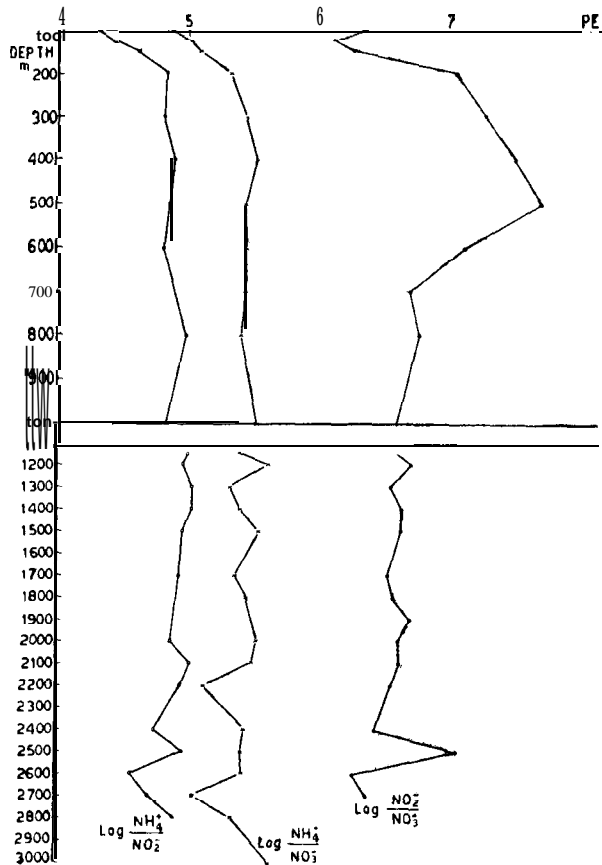


Fig. 2 — Equilibrium conditions of inorganic nitrogen system in the northern Arabian Sea (average of all *pE* values)

Arabian Sea. It is seen from the figure that nitrite has a maximum between 400 and 700 m. *pE* values for the redox pair  $\text{NO}_2^-/\text{NO}_3^-$  increase in this layer of sea water. Ammonia being absent or present in very low concentration is perhaps in the nitrite stage of its oxidation to nitrate and eventually to nitrogen gas. Below this depth the value for the redox pair  $\text{NO}_2^-/\text{NO}_3^-$  decreases i.e. the oxidation intensity increases with depth. Below 700 m this redox pair approaches a value which could be at equilibrium at the measured *pH* and temperature.

Values for the redox pair  $\text{N}_2/\text{NHO}_2^-$  increase down to 1200 m below which depth it shows a gradual decrease. It has been suggested that in the Indian Ocean, like the other oceans, the layer of maximum oxidation intensity lies around 1000-1500 m. This is indicated by decreasing ammonia and increasing nitrate and oxygen concentrations.

The values for the redox pair  $\text{NH}_4^+/\text{NO}_2^-$  do not show much variation with depth. This is expected because both  $\text{NO}_2^-$  and  $\text{NH}_3$  concentrations are very low and  $\text{NH}_3$  and  $\text{NO}_2^-$  being at intermediate stages in the inorganic nitrogen system do not approach equilibrium values.

The calculated values of *pE* for the redox pair  $\text{NH}_4^+/\text{NO}_3^-$  are plotted against the measured values of *pH* (Fig. 3). A *pE-pH* diagram shows how protons and electrons can simultaneously shift the equilibrium under various conditions and can indicate which of the species predominates under

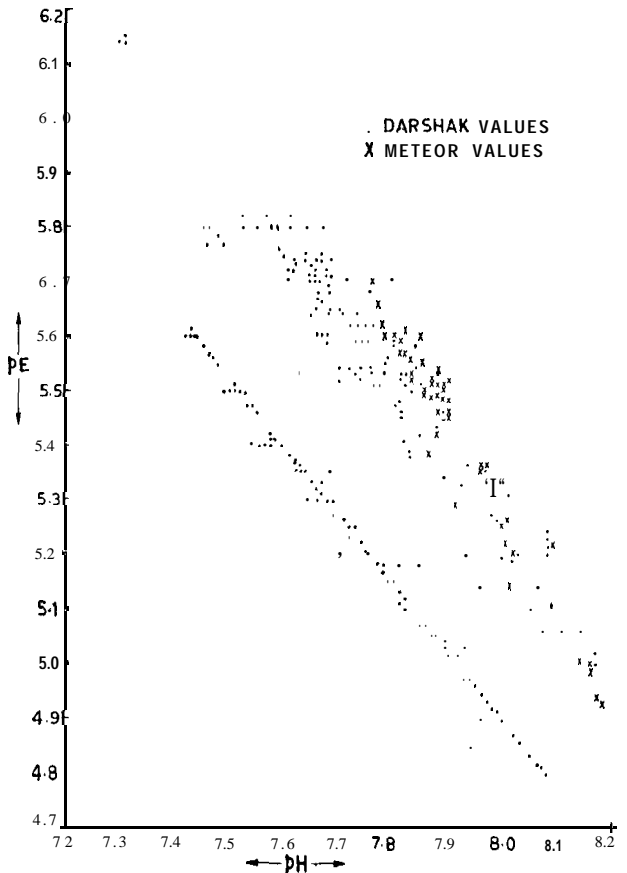


Fig. 3 — *pE-pH* diagram for the redox pair  $\text{NH}_4^+/\text{NO}_3^-$  in the Arabian Sea from *Darshak* and *Meteor* values

any given condition of  $pE$  and  $pH$ . The relation in Fig. 3 is linear but it is of 2 different orders depending on the concentrations of nitrate. It is relevant here to refer to the observed decrease of nitrate from south to north in the Arabian Sea<sup>11</sup>.

The plot 'a' is of values mostly from stations north of 20°N latitude and the plot 'b' is of values from south of the latitude. Values from the *Meteor* cruise fit well with plot 'b', confirming this latitudinal increase, as the *Meteor* values are from a section between 2°N and 3°S along 58°E across the equator. It is observed that from 100 to about 500 m, between  $pH$  7.75 and 8,  $pE$  values are between 5.2 and 4.9 while the equilibrium values for this redox pair in the observed  $pH$  range are between 5.2 and 5.6. This is mostly because of low nitrate concentrations in this layer. In the plot 'b' the same range of value has been observed also but at a comparatively higher range of  $pH$ . It has been suggested that in this layer denitrification may remove nitrate as nitrogen gas<sup>12</sup>. High nitrite associated with low oxygen has been observed in this layer<sup>12-14</sup> which has been termed as an azoic zone<sup>15</sup>.

From Eqs. (1-3) the equilibrium  $pE$  values for the 3 redox pairs at  $pH$  7 and 8 were calculated and are given below along with the ranges calculated from the data at the observed  $pH$  values.

Redox pair	$pH$ 7	$pH$ 8	Observed range
$NO_3^-/NO_2^-$	7.2	6.2	6.13-9.00
$NH_4^+/NO_3^-$	6.1	4.9	4.86-5.64
$NH_4^+/NO_2^-$	5.8	4.5	4.32-4.77

It is apparent from the above that these values lie quite close to the equilibrium  $pE$  values at  $pH$  7 and 8. Since the observed  $pH$  range of the depth levels investigated lies between 7 and 8, it may be concluded that the system  $NO_3^-/NO_2^-/NH_4^+$  in the sea is approximately in a state of near-equilibrium. But the values for the constants in the calculations of the relations for  $pE$  are at 25°C whereas, it is well known, that the average sea water is much colder. Also the system is assumed to be at atmospheric pressure.

In the sea nitrogen exists mainly as  $N_2(g)$  whereas at equilibrium with  $H_2O$  at  $pE$  12.5 and  $pH$  8.1 it should have been converted to  $NO_3^-$  in the ocean, in the regulation of the present composition of air and sea water<sup>16</sup>. In Sillén's model with  $pE$  at +12.5 this presented a dilemma, for most of the N should be found as  $NO_3^-$  instead of  $N_2$ . The anomaly was rationalized by assuming that the formation of  $NO_3^-$  from  $N_2$  was blocked kinetically by the high energy requirement to break the  $N\equiv N$  bond. However, at  $pE$  +8.5 the dominant form should be  $N_2$  with  $NO$ ; permitted at a low level of about  $10^{-6}M$ , in fact very much as actually found in the real sea<sup>4</sup>. Our values of  $pE$  do not differ much from the normal  $pE$  of sea water of 8.5, as suggested by Breck<sup>4</sup>, and the concentrations of nitrate varied from  $0.2 \times 10^{-6}$  to  $0.8 \times 10^{-6}M$ . It is very probable, therefore, that at intermediate layers, where denitrification takes place, most of the inorganic nitrogen compounds are converted to gaseous nitrogen in the northern Arabian Sea. But the present values are far from the value of 12.5 for  $pE$  as calculated by Sillén<sup>2</sup>. A

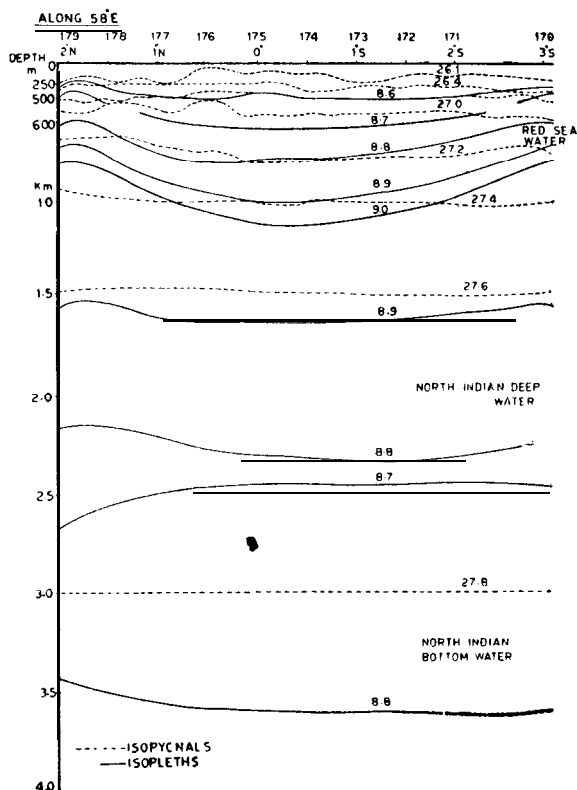


Fig. 4 — Isopycnals and isopleths for the redox pair  $NO_3^-/NO_2^-$  in equatorial Indian Ocean (from *Meteor* data)

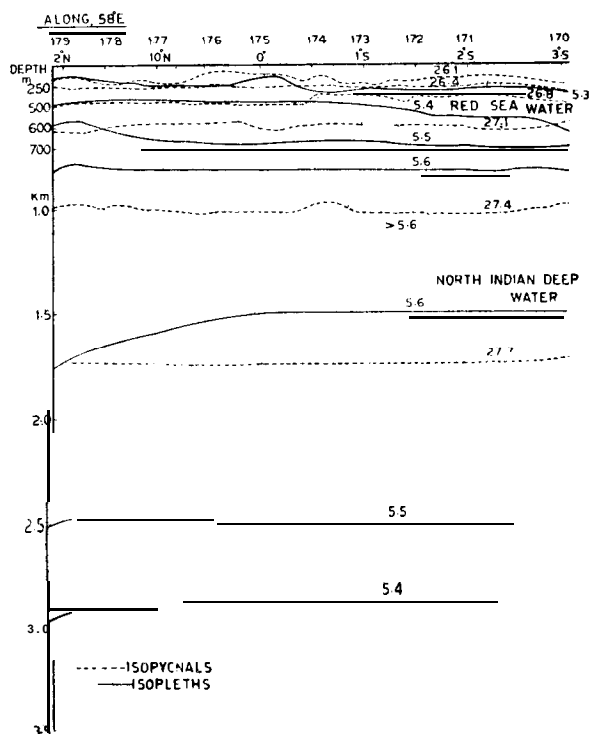


Fig. 5 — Isopycnals and isopleths for the redox pair  $NH_4^+/NO_2^-$  in equatorial Indian Ocean (from *Meteor* data)

system cannot have different  $pE$  values for different redox pairs and all of them should not differ much from one another. Considering the range of values obtained in the present calculations for the inorganic nitrogen system and considering all the influences that may be expected from temperature and pressure, it appears to us that Breck's suggestion may not be very different from the natural conditions in marine environments.

**Environmental** — To test the applicability of the values of the redox pairs for the study of characteristics of water masses, we plotted  $\sigma_t$  values along a meridional section at 58°E between 2°N and 3°S across the equator from *Meteor* data together with the  $pE$  values calculated by applying the  $\text{NO}_2^-/\text{NO}_3^-$  and  $\text{NH}_4^+/\text{NO}_3^-$  relationships (Figs. 4 and 5). The redox pair  $\text{NH}_4^+/\text{NO}_2^-$  was omitted since it is the intermediate stages in the inorganic nitrogen system and consequently far from equilibrium conditions. Fig. 4 shows the relationship between the isopycnals and the isopleths of  $\text{NO}_2^-/\text{NO}_3^-$  for depths greater than 250 m.  $pE$  values increase with depth indicating the increase in the intensity of oxidation. It appears that chemically the waters of the north-western Indian Ocean can be treated as a single water body where oxidation intensities increase gradually with depth. A maximum can be observed at a depth of 1000 m and at a  $\sigma_t$  value of 27.4. This is roughly the depth level of flow of Red Sea water in the equatorial region of the Indian Ocean. Below this depth  $pE$  values decrease. Maximum oxidation intensity in the oceans occurs at around 1000-1500 m depth. Present values of  $pE$  agree well with this conclusion. Thus the Red Sea water mass in the equatorial Indian Ocean can be distinguished from the waters above and below by the higher values of  $pE$ .

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