

perature the percentage retained in the crystal as  $\text{KMn}^*\text{O}_4$  has risen to about 50%.

4. A rapid interchange of a  $3d$  electron occurs between  $\text{MnO}_4^-$  and  $\text{MnO}_4^+$  ions.

5. In the case of  $+5$  phosphorus molecules and ions the recoils seem to eject oxidized oxygen leaving  $+3$  phosphorus about half of the time. The retention of activity is near 50% under all conditions.

6. Both  $+3$  and  $+5$  arsenic appear to expel  $-2$  divalent oxygen. The retention is nearly 100% under all conditions.

7. All the halate ions appear to be reduced by expulsion of  $-1$  or atomic oxygen, further substantiating a rough rule that the results of the

recoils will correspond to *distribution of the bonding electrons among the products about as they are distributed in the bonds broken.*

8. The halate ions interchange with the molecular halogens in acid solution, the rates increasing from chlorine to iodine. Perchlorate ion does not interchange rapidly with chlorine.

9. The organic halides have high retentions in the pure state due to collisions between the recoiling  $\text{X}^*$  particles and the halide molecules transferring the energy to non-radioactive atoms, generally halogens, and leaving the residual free radical or ion in the same reaction "cage" with the stopped  $\text{X}^*$  particle.

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## Some Properties of Monoethanolamine and its Aqueous Solutions

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Because of the varied and extensive use of monoethanolamine a more complete knowledge of its properties may be of considerable use. This paper affords data on the melting point, boiling point, refractive index, also the density, surface tension, parachor, and the surface tension of aqueous solutions over the temperature range 25 to 80°.

**Purification of Monoethanolamine.**—Samples from two sources, Eastman Kodak Company and Carbide and Carbon Chemicals Corporation, were subjected to fractional distillation, washed repeatedly with ether, and then crystallized from an ethyl alcohol solution. This was followed by fractional distillation, care being taken to prevent absorption of carbon dioxide. Two successive crystallizations and distillations gave, from each original sample, a product with constant melting point 10.51° (cor.). The boiling point was  $171.1 \pm 0.1^\circ$  at 760 mm. pressure; previous values reported are  $171.1^{11}$  and  $170.5^{12}$ .

As a further check on the purity of the monoethanolamine, it was analyzed by potentiometric titration against standard hydrochloric acid using a quinhydrone electrode and by weight titration using methyl orange indicator; the results were 99.97 and 99.96%, respectively.

The refractive index was found to be 1.4539 at 20° by the use of an Abbe refractometer.

**Density, 25 to 80°.**—Density determinations were made at 10° intervals from 25 to 80° with ordinary pycnometers which had very careful volume calibration. A water-bath controlled to within 0.05° of the desired temperature was

used. The monoethanolamine was freshly distilled before each determination. Results from the use of three 25 ml. pycnometers were compared; agreement within 0.005% was deemed satisfactory.

The results, tabulated in Table I, show the absolute density to be a linear function of the temperature. This relationship between density and temperature (°C.) is expressed by the equation,  $d = 1.03188 - 0.0008038 t$ . The average deviation of the points in Table I from values calculated by this equation is 0.000077.

TABLE I

DENSITY OF MONOETHANOLAMINE FROM 25 TO 80°	
Temperature, °C.	Density
25	1.01170
30	1.00773
40	0.99983
50	.99182
60	.98366
70	.97551
80	.96749

**The Surface Tension of Monoethanolamine from 25 to 80°.**—The surface tension of monoethanolamine was determined using the capillary rise method. The capillaries were made of Pyrex glass according to the design of Richards and his co-workers<sup>3</sup> and were fitted with ground glass stoppers to prevent the absorption of carbon dioxide and water vapor. The capillary tubing was inspected for uniformity of bore, and the radii of the capillaries were determined by the method of Harkins and Brown.<sup>4</sup> The values for the radii were checked by determining the capillary rise of water in the capillaries,

(1) Trusler, *Ind. Eng. Chem.*, **21**, 685 (1929).

(2) McClure, *Ind. Eng. Chem., News Ed.*, **17**, 149 (1939).

(3) Richards and co-workers, *THIS JOURNAL*, **37**, 1656 (1915).

(4) Harkins and Brown, *ibid.*, **41**, 449 (1919).

using the value of Harkins for the capillary constants of water at 25°. The results obtained in this manner checked those from the mercury measurements very closely throughout. The capillaries were cleaned with chromic acid cleaning solution, and were steamed out thoroughly and dried in an electric oven. The cathetometer used in measuring the capillary heights could be read to 0.02 mm. and the observed heights were corrected for the height of the meniscus in the capillary by the method of Richards.<sup>5</sup>

The measurements were made in a water thermostat controlled to within 0.05° of the desired temperature.

The results, tabulated in Table II, show the surface tension to be a linear function of the temperature. The surface tension-temperature (°C.) relationship is expressed by the equation,  $\gamma = 51.11 - 0.1117 t$ ; the average deviation of experimental points in Table II being 0.024 dyne.

TABLE II  
SURFACE TENSION AND TOTAL SURFACE ENERGY OF  
MONOETHANOLAMINE FROM 25 TO 80°

Temp., °C.	Surface tension, dynes	Total surface energy, $\mu$ , ergs
25	48.30	81.61
30	47.79	81.65
40	46.59	81.57
50	45.59	81.69
60	44.41	81.62
70	43.29	81.62
80	42.18	81.63

**Parachor.**—A determination was made of the parachor as developed by the work of MacLeod<sup>5</sup> and of Sugden,<sup>6</sup>

$$P = \frac{\gamma^{3/4}}{(d_l - d_v)} M \quad (2)$$

where  $\gamma$  is the surface tension in dynes,  $M$  is the molecular weight, and  $d_l$  and  $d_v$  are the densities of the liquid and its vapor, respectively. The range of temperature was 25 to 80°. The data given in Table III show that the parachor does not change markedly with temperature. The mean of the determinations, 160.0, compares favorably, dif-

ference 1.1%, with a calculated value, 161.8, using Sugden's data for the elements and groups: nitrogen, 12.5; hydrogen, 17.1; oxygen, 20.0; and the CH<sub>2</sub> group, 39.0. The amines in general show a more or less consistent difference of 1 to 4% between the observed and calculated values.<sup>6</sup>

TABLE III  
PARACHORS OF MONOETHANOLAMINE FOR TEMPERATURES  
25 TO 80°

Temp., °C.	Parachor
25	159.1
30	159.4
40	159.6
50	160.0
60	160.3
70	160.6
80	160.9

**Surface Tension of Monoethanolammonium Hydroxide Solution at 25°.**—The surface tension of a series of aqueous solutions of monoethanolamine (monoethanolammonium hydroxide) were determined at 25° by the capillary rise method. The results, see Table IV, indicate that this substance is quite capillary inactive.

TABLE IV  
SURFACE TENSION OF MONOETHANOLAMMONIUM  
HYDROXIDE SOLUTIONS AT 25°

Concn., molar	Surface tension, dynes
0.00100	71.37
.01950	71.37
.03000	71.35
.06000	71.26
.10000	71.00

### Summary

Data have been presented for the following properties of monoethanolamine: melting point, boiling point, refractive index, surface tension and parachor; also the surface tension of aqueous solutions at concentrations 0.1  $M$  and below.

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(5) MacLeod, *Trans. Faraday Soc.*, **19**, 38 (1923).

(6) Sugden, *J. Chem. Soc.*, **125**, 32, 1167, 1177 (1924); **127** 1868 (1925).