

Fig. 2.—Effect of temperature on solubilities in relation to volume:  $\nabla$ , methyl amyl ketone;  $\circ$ , diisopropyl ketone;  $\square$ , dipropyl ketone.

may be stretched out at low temperatures so that the  $\text{CH}_2$  groups are surrounded by the maximum possible number of water molecules, the attractive forces between these groups and water thus adding to the main interaction between the carbonyl dipole and water. When the temperature increases, the molecule may assume other more compact configurations which will be such as to decrease the number of water molecules adjacent to the  $\text{CH}_2$  groups. On the other hand, molecules such as that of diisopropyl ketone having compact branched structures can only assume a lim-

ited number of configurations and, hence, their solubilities are less temperature dependent.

### Summary

The solubilities in water of dipropyl, diisopropyl and methyl *n*-amyl ketones have been determined at various temperatures from 10 to 75° and vapor solubilities have been computed.

Free energies, heats and entropies of solution have been calculated. Additional evidence was obtained which tends to confirm the previous suggestion that equality of solute volume as well as chemical similarity is necessary for a linear relation to exist between entropies and heats of solution.

Large solubility differences and a large temperature dependence of these differences were noted in agreement with those previously found for other isomeric ketones.

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## The Surface Tension of Solutions of Electrolytes as a Function of the Concentration. IV. Magnesium Sulfate

BY GRINNELL JONES AND WENDELL A. RAY

This paper is a continuation of work previously reported<sup>1</sup> on the surface tensions of aqueous solution of electrolytes relative to that of pure water. These earlier papers should be consulted for a description of the experimental technique and a discussion of the historical and theoretical background of the problem. The data given are "apparent relative surface tensions" in the sense defined in the second paper of this series.

Magnesium sulfate was chosen for this work because none of the salts already studied belonged to this valence type. The measurements have been carried out at 25.00° over a concentration range of 0.0001 up to 2 molar.

Analytical reagent grade magnesium sulfate was purified by two recrystallizations from water. The crystals were washed by centrifugation and

slowly dried in an electric oven. As the salt was hygroscopic each sample before final weighing was kept in an electric furnace at 475° for several hours or until constant weight was assured. At this temperature the anhydrous salt was formed. The samples were weighed in platinum boats in stoppered weighing bottles. A saturated solution showed no red coloration with phenolphthalein. Two 50-ml. Ostwald type pycnometers were used for the density measurements and gave duplicate results differing by not more than a few parts per million. The surface tension measurements were made by the differential capillary rise method as described in the first and second papers of this series. The figures given in Table I are the mean of at least two independent determinations for each concentration. The results are shown graphically in Figs 1 and 2.

(1) Grinnell Jones and Wendell A. Ray, *THIS JOURNAL*, **59**, 187 (1937); **63**, 288, 3262 (1941); Grinnell Jones and L. D. Frizzell, *J. Chem. Phys.*, **8**, 986 (1940).

TABLE I  
DENSITY AND APPARENT RELATIVE SURFACE TENSION OF  
MAGNESIUM SULFATE SOLUTIONS AT 25°

Concentration, molar	Density $d_{25}^4$	Apparent rela- tive surface tension	$(\sigma_c - \sigma_0)/\sigma_0$
0.000100	0.997085	0.99997	-0.3
.000200	.997096	.99994	- .3
.000500	.997131	.99993	- .14
.001000	.997190	.99997	- .03
.002000	.997322	1.00003	+ .15
.005000	.997694	1.00022	+ .044
.010000	.998319	1.00046	+ .046
.020000	.999544	1.00087	+ .0435
.050000	1.003198	1.00195	+ .0390
.10000	1.009195	1.00345	+ .0345
.20000	1.021005	1.00638	+ .0319
.49647	1.055099	1.01435	+ .02890
1.0000	1.110781	1.02836	+ .02836
1.98720	1.214289	1.06603	+ .03323

### Interpretation of the Data

The densities of magnesium sulfate may be expressed over the range studied by an equation of the form suggested by Root.<sup>2</sup>

$$d_{25}^4 = 0.997074 + 0.124469c - 0.010756c^{3/2}$$

This equation agrees with the data with an average deviation of less than 0.001%.

From the curve it may be seen that the apparent relative surface tension of magnesium sulfate in the extreme dilute range becomes less than unity giving a minimum. The surface tension at the minimum is about 0.010% below that of pure water. The minimum occurs at about 0.0005 molar. This minimum is similar to that found by us for the other salts studied. At higher concentrations the surface tension is nearly a linear function of the concentration but a slight positive curvature may be noted at the highest concentrations which has been found typical of all the salts studied in this Laboratory in the past.

(2) W. C. Root, *THIS JOURNAL*, **55**, 850 (1933).

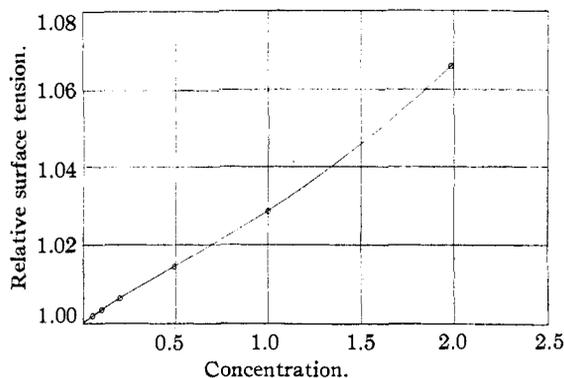


Fig. 1.

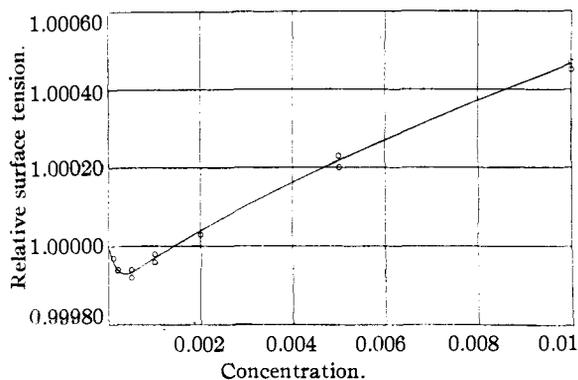


Fig. 2.

### Summary

The apparent relative surface tensions of aqueous solutions of magnesium sulfate have been measured from 0.0001 to 2 molar at 25.00°.

At extreme dilution magnesium sulfate apparently gives a minimum in the surface tension-concentration curve. This same type of minimum has been observed for all of the other salts so far reported in this series.

At moderate and high concentrations magnesium sulfate increases the surface tension of water almost linearly with concentration and behaves as a typical "capillary-inactive" substance.

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