7. The rotation of the ethyl groups of *n*-butane is hindered by a potential of the order of 30,000 cal./mole.

8. It is shown that reliable thermodynamic functions for *n*-butane at high temperatures may be obtained despite uncertainty in the vibrational frequency assignment.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, GREENSBORO COLLEGE]

Aqueous Solubilities of Some Aliphatic Ketones

BY P. M. GINNINGS, DOROTHY PLONK AND ELOISE CARTER

In view of the dearth of information in the literature as to the solubility in water of aliphatic ketones and the relationships already found between the molecular structure and solubility of aliphatic alcohols,[1] the aqueous solubilities of twelve such ketones have now been measured.

The solubilities (Table I) were determined by the same volumetric method as was used for the alcohols, and are considered accurate to within 0.05 weight per cent. except that 0.20 weight per cent. should probably be allowed in nos. 1 and 2. The ketones were of the best Eastman Kodak Co. grade except nos. 5, 8, 9 and 10, which were prepared from the corresponding secondary alcohols by the method of Yohe.[2] All were purified by fractional distillation through a 1-meter column, usually from barium oxide. Nos. 1, 3, 6, 8 and 12 were further purified by means of sodium bisulfite.

TABLE I

No.	d^{25}_4 of pure ketone and b. p. °C. (760 mm.)	Temp., °C.	Wt. % ketone		d^{20}_4, $^{25}_4$, $^{30}_4$ of the liquid phases Water rich	Ketone rich
			Butanone-2			
1[a,b]	0.8007	20	27.33	88.41	0.9620	0.8353
	80.7–80.8	25	25.57	88.28	.9611	.8322
		30	24.07	88.15	.9615	.8270
			3-Methylbutanone-2			
2	0.8189	20	6.53	97.61	.9908	.8328
	93.1–94.0	25	6.08	97.43	.9901	.8284
		30	5.68	97.24	.9890	.8238
			Pentanone-2			
3	0.8018	20	5.95	96.70	.9903	.8147
	102.2–102.3	25	5.51	96.52	.9897	.8103
		30	5.18	96.32	.9887	.8059
			Pentanone-3			
4[c]	0.8116	20	5.08	98.55	.9925	.8195
	101.6–101.9	25	4.81	98.38	.9915	.8150
		30	4.50	98.17	.9901	.8108
			3-Methylpentanone-2			
5	0.8083	20	2.26	98.05	.9926	.8328
	117.4–117.5	25	2.09	97.97	.9944	.8131
		30	1.93	97.83	.9935	.8088
			4-Methylpentanone-2			
6	0.7969	20	2.04	97.59	.9951	.8092
	115.6–115.7	25	1.91	97.93	.9944	.8018
		30	1.78	97.80	.9932	.7981
			3,3-Dimethylbutanone-2			
7	0.8012	20	2.04	98.35	.9954	.8097
	106.0–106.1	25	1.90	98.24	.9946	.8053
		30	1.77	98.14	.9933	.8010
			Hexanone-2			
8	0.8072	20	1.75	97.88	.9959	.8154
	127.5–127.6	25	1.64	97.75	.9950	.8117
		30	1.53	97.64	.9938	.8079
			4-Methylpentanone-3			
9	0.8059	20	1.63	98.79	.9959	.8128
	115.0–115.1	25	1.52	98.69	.9952	.8088
		30	1.42	98.60	.9941	.8047
			Hexanone-3			
10	0.8111	20	1.57	98.47	.9962	.8175
	123.6–123.7	25	1.47	98.38	.9952	.8134
		30	1.38	98.30	.9943	.8087
			2,4-Dimethylpentanone-3			
11	0.7900	20	0.59	99.24	.9976	.8044
	125.4–125.5	25	.57	99.19	.9966	.8003
		30	.56	99.15	.9953	.7962
			Heptanone-2			
12	0.8115	20	0.44	98.69	.9978	.8177
	151.2–151.3	25	.43	98.59	.9967	.8141
		30	.40	98.48	.9953	.8098

[a] Park and Hofman, *Ind. Eng. Chem.*, 24, 134 (1932), give data for Nos. 1, 3, 8 and 12 at room temperatures (about 25°). [b] Evans, *Ind. Eng. Chem. Anal. Ed.*, **8**, 208 (1936), has measured no. 1 at 20° using a volumetric method obtaining 26.7 wt. %. [c] Gross, Saylor and Gorman, THIS JOURNAL, **55**, 650 (1933), have measured no. 4 accurately at 30°, obtaining 4.48 wt. %.

Discussion

The most important factor is of course the molecular size (nos. 1, 3, 8 and 12) as the smallest ketone is the most soluble (acetone is soluble in water in all proportions). In a group of isomeric ketones, solubility tends to increase as molecular structure becomes more compact (nos. 3 and 2; 10 and 9; 8, 6, 5 and 7). Most unexpected was the effect of the position of the carbonyl group. In alcohols increasing solubility follows move-

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[1] For instance, unsaturated alcohols, Ginnings, Herring and Coltrane, THIS JOURNAL, **61**, 807 (1939).

[2] Yohe, Lauder and Smith, *J. Chem. Education*, **10**, 374 (1933).

ment of the hydroxyl group toward the center of the molecule but in these ketones, the carbonyl group tends to decrease the solubility as it is moved toward the center (nos. 3 and 4; 6 and 9; 8 and 10). The effect of the carbonyl position is especially noticeable in the case of no. 7, resulting in an unexpected decrease in the solubility (nos. 8, 6, 5 and 7). These ketones all become less soluble with increasing temperature.

Summary

Aqueous solubilities of twelve aliphatic ketones have been determined for 20, 25 and 30°. Low molecular weights and low temperatures result in large solubilities. The most compact isomers tend to be most soluble but movement of the carbonyl group toward the center of the molecule tends to reduce the aqueous solubility.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE RICE INSTITUTE]

The Electrolyte Coagulation Process: the Influence of Dilution of Sol on the Adsorption of Precipitating Ions

BY HARRY B. WEISER AND W. O. MILLIGAN

The concentration of electrolytes required to coagulate hydrophobic sols varies with the concentration of sol, a phenomenon first observed by Mukopadhyaya.[1] Burton and Bishop[2] formulated the rule that, in general, the precipitation value of univalent precipitating ions increases with dilution of sol; that of bivalent ions is almost constant and independent of the sol concentration; and that of trivalent ions decreases with the sol concentration. Weiser and Nicholas[3] pointed out that Burton and Bishop's rule is not generally applicable since with many sols, especially those of the hydrous oxides, the precipitation value of electrolytes decreases with dilution of sol irrespective of the valence of the precipitating ion. Sorum[4] showed, however, that certain hydrous oxide sols which do not follow Burton and Bishop's rule when relatively impure will obey the rule after sufficient purification by dialysis, but no explanation is offered for this behavior.

Because of the limitations of rules of electrolyte coagulation which attempt to formulate the conditions for reducing the potential on the dispersed particles to a critical value, Ostwald[5] introduced the principle that the dispersion medium rather than the colloidal particles should be in a corresponding (in the simplest case identical) physical-chemical state for coagulation to take place. It is argued that coagulation should take place at the same activity coefficient of the precipitating ion (f^+ for negative sols and f^- for positive sols) irrespective of the salt employed. The activity coefficient of a single cation, for example, is given in accord with the Debye–Hückel theory by a relation of the form $-\log f^+ = 0.5\,(z^+)^2\sqrt{u/n^+}$, in which z is the valence of the cation, n^+ the number of cations in the molecule and u is the ionic strength which is given by the expression $u = 0.5\,[m^+(z^+)^2 - m^-(z^-)^2]$, where m^+ and m^- are the molarities of the cation and anion, and z^+ and z^- are the valences of the respective ions in the coagulating electrolyte.

Ostwald's simple formulation, f^+ (or f^-) = constant, is necessarily limited in its applicability.[6] In the first place, the precipitation values of electrolytes vary in different ways with dilution of sol so that in general the activity coefficient of the precipitating ion at the coagulation value cannot be constant over any wide range of concentration. In the second place, if Ostwald is right that the dispersion medium should be in the same physical-chemical state for coagulation to take place, then the activity coefficients of the precipitating ions in equilibrium with the particles should be compared rather than the activity coefficients calculated on the basis of the total amount added to effect coagulation. If such a comparison is made there is no reason to believe that the critical activity coefficients will approach a constant value for ions of varying valence since only a small percentage of univalent ions is adsorbed at their precipitation value whereas a large percentage of most multi-

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(1) Mukopadhyaya, THIS JOURNAL, **37**, 2024 (1915); Kruyt and van der Spek, *Kolloid. Z.*, **25**, 3 (1919).

(2) Burton and Bishop, *J. Phys. Chem.*, **24**, 701 (1920); Burton and MacInnes, *ibid.*, **25**, 517 (1921).

(3) Weiser and Nicholas, *ibid.*, **25**, 742 (1921).

(4) Judd and Sorum, THIS JOURNAL, **52**, 2598 (1930); Fisher and Sorum, *J. Phys. Chem.*, **39**, 283 (1935); **44**, 62 (1940).

(5) For a survey with references see *ibid*, **42**, 981 (1938).

(6) *Cf.* Weiser, "Inorganic Colloid Chemistry," Vol. III, John Wiley and Sons, New York, N. Y., 1938, pp. 190 *et seq.*