207. *Conductimetric Studies in Ketonic Solvents. Part II.* Water in Ketones.*

By S. R. C. Hughes.

The density and viscosity data for acetone containing water can be correlated with the water content by linear equations; similar correlations have been made for ethyl methyl ketone containing water. The conductivity data for potassium iodide in acetone and in ethyl methyl ketone, related to water content, show contrasting rôles of water in these two media.

Correlation of Physical Data.—In Part I * it was inferred that conductivity measurements hitherto made in acetone are modified by the presence of considerable proportions of water. These studies are now extended so as to permit comparison between this solvent and ethyl methyl ketone.

The available density and viscosity data at 25° for acetone containing up to 5% of water can be summarized by the linear equations (1) and (2) (where x is the weight %

$$d_4^{25} = 0{\cdot}78345 + 0{\cdot}003067x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\eta_0^{25} = 0{\cdot}003000 + 0{\cdot}0001667x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

of water), as shown by the correlations in Table 1.

Table 1. *Physical data for acetone–water mixtures at* 25°.

Source	x (H_2O, %)	d_4^{25}	Deviation from Eqn. (1)	$10^4\eta_0^{25}$	Deviation from Eqn. (2)
Part I	$0{\cdot}18$	$0{\cdot}7840_0$	$0{\cdot}0000_0$	—	—
,,	$0{\cdot}22$	$0{\cdot}7841_3$	$0{\cdot}0000_1$	—	—
Ref. 1	$(0{\cdot}34_2)$	$0{\cdot}7845$	—	$30{\cdot}40$	$-0{\cdot}000017$
Ref. 2	$0{\cdot}45$	$0{\cdot}7849$	$0{\cdot}0000_7$	$32{\cdot}00$	$0{\cdot}00012_5$
Ref. 3	$(0{\cdot}46_6)$	$0{\cdot}7848_8$	—	$30{\cdot}93$	$0{\cdot}00001_5$
Ref. 4	$(0{\cdot}51_5)$	$0{\cdot}7850_3$	—	$30{\cdot}7_5$	$-0{\cdot}00001_1$
Ref. 4	$0{\cdot}76_5$ *	$0{\cdot}7858_7$	$0{\cdot}0000_7$	$30{\cdot}9_5$	$-0{\cdot}00003_2$
Part I	$0{\cdot}87$	$0{\cdot}7861_2$	$0{\cdot}0000_1$	—	—
Ref. 5	$(0{\cdot}89_7)$	$0{\cdot}7862$	—	$31{\cdot}5_8$	$0{\cdot}00000_8$
Ref. 4	$1{\cdot}00_8$ *	$0{\cdot}7865_1$	$-0{\cdot}0000_1$	$31{\cdot}2_0$	$-0{\cdot}00004_8$
,,	$1{\cdot}51_1$ *	$0{\cdot}7880_2$	$-0{\cdot}0000_7$	—	—
Part I	$1{\cdot}65$	$0{\cdot}7882_2$	$-0{\cdot}0002_9$	—	
Ref. 2	$2{\cdot}89$	$0{\cdot}7922$	$-0{\cdot}0001_2$	$34{\cdot}9$	$0{\cdot}00000_8$
,,	$5{\cdot}35$	$0{\cdot}7997$	$0{\cdot}0001_6$	$37{\cdot}8$	$0{\cdot}00011_2$

* Water contents in parentheses are calculated from the authors' densities by Eqn. (1). Those marked with asterisks refer to wetted acetones in which such initial water contents are included. All other water contents are based upon analyses by Karl Fischer's method.

Density and viscosity data determined here for wetted ethyl methyl ketone containing up to 4·728% of water may similarly be summarized by equations (3) and (4), whose correlation is illustrated in Table 2.

$$d_4^{25} = 0{\cdot}79978 + 0{\cdot}002645_8x \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$\eta_0^{25} = 0{\cdot}003792 + 0{\cdot}0001275x \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The relative dielectric constants of ethyl methyl ketone–water mixtures at 25° are found to be adequately reproduced up to 5% of water by equation (5) :

$$D = 18{\cdot}4 + 0{\cdot}701x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Conductivity of Potassium Iodide in Wetted Acetone and in Wetted Ethyl Methyl Ketone.—In Part I are given the Λ_0 and K values for potassium iodide in acetone samples of reported

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* Part I, *J.*, 1954, 953.

[1] Reynolds and Kraus, *J. Amer. Chem. Soc.*, 1948, **70**, 1709.
[2] Olsen and Konecny, *ibid.*, 1953, **75**, 5801.
[3] International Conference (Brussels), *J. Chim. phys.*, 1928, **25**, 401.
[4] Data of Ross-Kane : Hartley and O. L. Hughes, *Phil. Mag.*, 1933, **54**, 975.
[5] Walden, Ulich, and Busch, *Z. phys. Chem.*, 1926, **123**, 429.

density, whose water contents can therefore be estimated by application of Equation (1). Data relating to potassium iodide in ethyl methyl ketone and mixtures of this solvent with water are reported in Tables 3 and 4, in which κ is the conductance of the solvent in mhos and c the concentration of potassium iodide in moles/l. It is thus possible to calculate Bjerrum parameters and Walden products for potassium iodide in these media, the data being summarized in Figs. 1 and 2.

TABLE 2. *Physical data for ethyl methyl ketone–water mixtures at 25°.*

x (H_2O, %)	d_4^{25}	Deviation from Eqn. (3)	$10^4\eta_0^{25}$	Deviation from Eqn. (4)
0 *	0·7995$_8$	−0·0002$_0$	37·9$_9$	0·00000$_7$
0 †	0·7997$_6$	−0·0000$_2$	38·1$_5$	0·00002$_3$
0·2031	0·8003$_2$	0·0000$_1$	38·3$_0$	0·00001$_2$
0·2474	0·8004$_1$	−0·0000$_2$	—	—
0·3329	0·8006$_8$	0·0000$_2$	—	—
0·4520	0·8009$_6$	−0·0000$_2$	38·4$_5$	−0·00000$_5$
0·4780	—	—	38·5$_6$	−0·00000$_3$
0·5100	0·8011$_3$	0·0000$_0$	—	—
0·5350	0·8012$_1$	0·0000$_1$	38·4$_9$	−0·00001$_1$
0·7333	—	—	38·8$_0$	−0·00000$_5$
0·8321	0·8017$_3$	0·0002$_5$	38·8$_0$	−0·00001$_8$
0·8676	0·8020$_9$	0·0000$_1$	39·1$_4$	0·00001$_1$
0·9060	—	—	39·1$_2$	0·00000$_4$
0·9519	0·80209	−0·0002$_1$	—	—
1·176	—	—	39·4$_0$	−0·00000$_2$
1·184	—	—	39·3$_7$	−0·00000$_7$
1·338	0·8032$_0$	−0·0001$_2$	39·2$_6$	−0·00003$_7$
1·700	0·8041$_5$	−0·0001$_3$	40·0$_3$	−0·00000$_6$
2·191	—	—	40·6$_5$	−0·00000$_6$
2·628	0·8065$_0$	−0·0002$_3$	41·1$_5$	−0·00001$_2$
3·588	0·8095$_0$	0·0002$_3$	—	—
4·713	—	—	44·0$_0$	−0·00000$_7$
4·728	0·8125$_1$	0·0002$_2$	43·8$_0$	0·00001$_4$

* Ethyl methyl ketone protected from laboratory atmosphere in the dry space. In the viscosity determinations, silica-gel guard tubes were fitted to the viscometer.

† Solvent handled in laboratory atmosphere. Guard tubes omitted from viscometer.

TABLE 3. *Conductivity of potassium iodide in dry ethyl methyl ketone at 25°.*

$D = 18{\cdot}4.^7$ By Fuoss plot: $\Lambda_0 = 150{\cdot}8$, $K = 2{\cdot}125 \times 10^{-3}$.

$10^8\kappa$	10^4c	Λ	$10^8\kappa$	10^4c	Λ	$10^8\kappa$	10^4c	Λ	$10^8\kappa$	10^4c	Λ
3·380	0·7132	142·0	3·841	2·803	129·5	2·808	4·777	122·6	3·841	6·455	117·8
2·808	0·8616	141·1	4·609	3·125	128·3	3·380	4·932	122·3	3·380	6·776	117·1
4·609	1·485	136·9	2·808	3·388	127·5	3·841	5·112	121·4	2·808	7·313	115·5
3·380	1·545	136·6	3·380	3·534	126·9	4·609	5·271	119·9	4·609	7·456	115·0
2·808	2·040	133·8	4·609	4·176	123·8	2·808	6·232	118·6	3·380	8·009	114·2
3·380	2·389	131·7									

TABLE 4. *Conductivity of potassium iodide in wetted ethyl methyl ketone at 25°.**

10^4c	Λ	10^4c	Λ	10^4c	Λ	10^4c	Λ	10^4c	Λ
$x = 0{\cdot}301\%$; $10^7\kappa = 0{\cdot}389$		$x = 0{\cdot}510\%$; $10^7\kappa = 0{\cdot}830$		$x = 0{\cdot}537\%$; $10^7\kappa = 0{\cdot}510$		$x = 0{\cdot}906\%$; $10^7\kappa = 0{\cdot}492$		$x = 0{\cdot}952\%$; $10^7\kappa = 1{\cdot}44$	
0·5614	142·1	0·2580	140·9	0·9928	138·5	0·8930	136·6	0·5830	139·1
1·213	137·4	0·7003	139·4	1·923	133·2	2·024	130·4	2·046	131·2
1·961	133·4	1·610	134·7	3·248	127·6	3·395	125·4	3·518	125·1
2·707	130·0	2·354	130·8	4·379	123·7	4·900	120·6	5·001	120·0
3·580	126·0	3·830	125·4	$\Delta_0 = 148{\cdot}4$; $10^3K = 2{\cdot}50_5$		7·160	115·1	6·627	116·1
$\Lambda_0 = 148{\cdot}8$; $10^3K = 2{\cdot}57$		$\Lambda_0 = 148{\cdot}2$; $10^3K = 2{\cdot}55_4$				$\Lambda_0 = 145{\cdot}2$; $10^3K = 2{\cdot}76_4$		$\Lambda_0 = 145{\cdot}6$; $10^3K = 2{\cdot}58_4$	

$x = 1{\cdot}338\%$; $10^7\kappa = 3{\cdot}63$		$x = 1{\cdot}700\%$; $10^7\kappa = 3{\cdot}20$		$x = 2{\cdot}628\%$; $10^7\kappa = 11{\cdot}27$		$x = 3{\cdot}588\%$; $10^7\kappa = 6{\cdot}10$		$x = 4{\cdot}728\%$; $10^7\kappa = 8{\cdot}11$	
1·042	133·3	0·9315	131·3	1·331	120·8	0·8441	121·4	0·6415	115·3
2·052	127·9	2·080	127·3	3·046	117·6	1·834	117·3	1·538	112·7
2·900	125·3	3·103	122·1	5·564	111·6	3·101	114·2	2·470	110·1
4·028	121·4	4·016	120·0	$\Lambda_0 = 132{\cdot}1$; $10^3K = 4{\cdot}06$		4·636	110·0	4·051	106·5
5·637	117·2	$\Lambda_0 = 139{\cdot}0$; $10^3K = 3{\cdot}45$				5·762	108·6	$\Lambda_0 = 120{\cdot}6$: $10^3K = 5{\cdot}08$	
$\Lambda_0 = 142{\cdot}5$; $10^3K = 2{\cdot}99_5$						$\Lambda_0 = 127{\cdot}4$; $10^3K = 4{\cdot}87_2$			

* Values of Λ_0 and K at the bottom of each section are obtained from the Fuoss plot.

EXPERIMENTAL

Conductivity Measurements and Purification of Solvents.—These followed the procedures previously described for Grade I acetone (Part I). Additions of conductivity water to dry ethyl methyl ketone were made from a weight burette. Densities were determined in a 100-c.c. graduated pyknometer designed for handling within the dry-space (*loc. cit.*). For viscosity measurement a Technico No. 0 viscometer was used; it was calibrated with water which gave a flow time of 22 min. 35·0 sec. at 25°. Except where otherwise stated (see footnotes to Table 2), the dry solvent and samples containing less than 1% of water were protected from the laboratory atmosphere by dry-space technique.

Dielectric Constants.—Comparative values for these for wetted samples of ethyl methyl ketone were measured on a heterodyne-beat bridge. The solvent was contained in a double-surface, silvered, condenser cell calibrated with dry ethyl methyl ketone for which the value $D_{25} = 18{\cdot}4$ was adopted.[7] Capacitances were measured by parallel replacement with a Muirhead precision air-condenser.

DISCUSSION

The contrasting physical interactions of acetone and of ethyl methyl ketone with water make it more practicable to obtain the latter ketone dry. The author believes that the alumina and dry-space techniques (described in Part I) have achieved this object; the physical data at the head of Table 2 and the conductivity of potassium iodide in the unwetted solvent confirm this view. The density reported by Walden and Birr [8] for their ethyl methyl ketone shows it to have contained $0{\cdot}69_2\%$ of water by Equation (3); the resultant viscosity from Equation (4) is in fair agreement with their value. The conductivity data for potassium iodide recorded by Walden and Birr, recalculated by Fuoss's method, show good correlation with values measured here in wetted ethyl methyl ketone (Figs. 1 and 2).

FIG. 1.

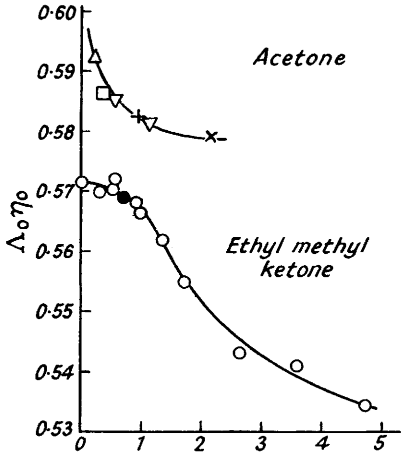

FIG. 2.

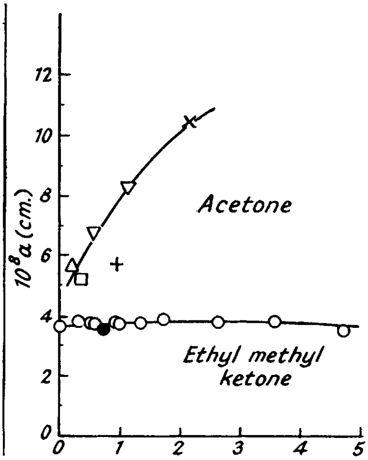

FIG. 1. *Walden product for potassium iodide in wet ketones at 25°.*
FIG. 2. *Bjerrum product for potassium iodide in wet ketones at 25°.*

○ Present work.
△ Part I.
□ Reynolds and Kraus.[1]
▽ Ross-Kane.[4]
+ Walden, Ulich, and Busch.[5]
× Bauer.[6]
● Walden and Birr.[8]

The Walden product ($\Lambda_0\eta_0^{25}$) for potassium iodide in acetone descends sharply with initial increase of solvent water content (Fig. 1). The behaviour reported for lithium bromide in these media is similar.[2] Such variations in acetone have been largely ascribed to increase in hydrodynamic cation radius.[4] The Bjerrum distance for potassium iodide

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[6] Bauer, *Ann. Physik*, 1930, **6**, 253.
[7] Sacks and Fuoss, *J. Amer. Chem. Soc.*, 1953, **75**, 5712.
[8] Walden and Birr, *Z. phys. Chem.*, 1931, *A*, **153**, 1.

in acetone also rises markedly with increase in water content of the solvent (Fig. 2). The Stokes and the Bjerrum parameters correspond, in this instance, closely enough for their mutual solution to be effected and their variations are consistent with a rapid increase in cation radius with increase in water content of the solvent (Part I).

In dry ethyl methyl ketone, the product $\Lambda_0\eta_0^{25}$ for potassium iodide is less than that found in the wettest acetone solution on record and remains practically constant over the first 1% of added water; from 1% to 3% it descends steeply, but less so for additions of water above 3%. The Bjerrum parameters for potassium iodide, both in dry ethyl methyl ketone and in solvent containing up to 4·7% of water, remain within 0·2 Å of the crystallographic distance for this salt. It is evident that there is no correspondence between Stokes and Bjerrum radii in these media, the former being considerably larger and showing some variation with water content of the solvent.

Disparity between Stokes and Bjerrum radii may be due to mathematical deficiencies, superimposed in some cases upon actual de-solvation caused by electrostatic association.[7,9–11] Agreement between the iodide radii, extracted in Part I, and the crystallographic value suggests that where these parameters are compatible the mathematical deficiencies may be small. If we assume, therefore, that some physical reality attaches to the two parameters in the cases analyzed here, the contrast between the two ketonic solvents becomes clearer.

The cationic solvation sheath for potassium iodide in moist acetone is a sufficiently stable structure to withstand ion association, and it increases with added water, the increase being the greater at lower water contents. That in dry, and in 1% wetted, ethyl methyl ketone, while greater than the acetone sheath radius by some 1 Å (with assumption of an unsolvated iodide ion, $r_{\text{I}^-} = 2{\cdot}16$ Å) is unable to withstand ion association. When ethyl methyl ketone is wetted up to 4·7% the hydrodynamic cation radius parameter attains approximately the value found in acetone containing $0{\cdot}51_5$% of water.

These comparisons indicate that the water contained in acetone is highly effective in solvating cations, whereas that in wetted ethyl methyl ketone is less so. Furthermore, the water in acetone solvates the potassium ion with a peculiar stability dependent, perhaps, on ionic co-ordination number. The re-analyzed conductivity data of Walden, Ulich, and Busch [5] and of Dippy, Jenkins, and Page [12] for sodium iodide in acetone show this salt to have a greater Stokes cation radius than potassium iodide but a smaller Bjerrum parameter, greater, however, than its crystallographic distance. Olsen and Konecny's observations [2] show a sharp increase in hydrodynamic radius on wetting lithium bromide in acetone, whereas the Bjerrum parameters remain close to the crystallographic distance up to 5% of total water content. It will be shown in a subsequent communication that relative alkali-cation association parameters, in dry ketonic solvents, stand in the reverse order to those in acetone.

Fuoss and his co-workers [7,9–11] find methanol to be a more effective solvating agent when depolymerized [13] by suitable diluents than when in its normal associated state. An analogous explanation of the contrasts seen here, between the behaviour of water in acetone and that in ethyl methyl ketone, seems reasonable. The high cation-solvating efficiency of water in acetone could be ascribed to the depolymerization of water by this solvent; the different rôle played by water in ethyl methyl ketone is consistent with its remaining associated in this medium. The contrasting physical interactions of these two ketones with water (*e.g.*, miscibility, vapour pressure) do not contradict this hypothesis.

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[9] Miller and Fuoss, *J. Amer. Chem. Soc.*, 1953, **75**, 3076.
[10] Sadek and Fuoss, *ibid.*, 1954, **76**, 5897.
[11] *Idem*, *ibid.*, p. 5905.
[12] Dippy, Jenkins, and Page, *J.*, 1939, 1386.
[13] Mecke, *Discuss. Faraday Soc.*, 1950, **9**, 161.