XVI.—*The Vapour Pressures of Mixtures of* (a) *Methyl Acetate and Water;* (b) *Methyl Acetate, Sucrose, and Water.*

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The measurements now recorded were carried out with the primary object of testing various "activity" theories of reaction velocity in the special case of the hydrolysis of methyl acetate by acids. Whilst no satisfactory conclusions could be drawn from their application in this connexion, the data may be of value from the point of view of thermodynamic theory, or they may be of use to other workers in the field of chemical kinetics.

The activities of the two volatile constituents in ester–water and ester–sucrose–water mixtures have been obtained by measurement of their partial vapour pressures, which represent the respective activities with sufficient accuracy for most purposes. As a check, the total vapour pressure of each system investigated has also been determined by an independent method. In the case of ester–water mixtures, concentrations of ester up to about $2N$ have been used. All the ester–sucrose–water mixtures contained a constant small concentration of ester, the sucrose content varying up to 600 g. per litre of solution. This involves a considerable variation in the concentration of water. All measurements have been carried out at two temperatures, *viz.*, 25° and 35°.

EXPERIMENTAL.

Total Vapour Pressures.—The static method of measurement adopted was very similar to that proposed by Morton (*J. Soc. Chem. Ind.*, 1919, **38**, 363T). A few practical modifications may be mentioned. In place of the jacketing arrangement indicated in Morton's diagram, the two barometer tubes and the capillary tubes attached to their upper ends pass through the bottom of a thermostat maintained at the working temperature. The lower ends of the barometer tubes dip below the surface of mercury in a closed container. This arrangement avoids the necessity for rubber joints and connexions and consequent fouling of the mercury. A small sealed glass stirrer containing a bundle of soft-iron rods is placed in the barometer tube which contains the experimental mixture. This stirrer, operated from outside by an electromagnet, facilitates the removal from the liquid of dissolved air, which is then pumped out through the capillary. Before the hydrostatic levels of mercury and solution in the tubes are read, the stirrer is lifted out of the solution and suspended above its surface by means of the electromagnet. The levels are read off through a telescope on an accurately graduated glass scale placed behind the tubes. In order to dispense with the precautions necessary to ensure a complete vacuum in the comparison tube (a trace of moisture in this would, of course, lead to erroneous results), it has been found convenient to retain a few c.c. of air-free water over the mercury surface in this tube. The vapour pressure of the mixture under examination is then compared, not against zero pressure, but against the pressure of saturated aqueous vapour at the same temperature. A glass tap at the end of the capillary tube attached to the comparison tube prevents the expulsion of this water at each pumping operation which is carried out for the other tube.

For the purpose of vapour-pressure measurements, the purest methyl acetate is essential. Kahlbaum's ester was therefore purified by the method recommended by Young and Thomas (J., 1893, **63**, 1191). The pure product distilled between 56·9° and 57·1° (standardised thermometer) at 760 mm. (Young and Thomas give 57·1°.) The vapour pressure of the pure ester was 214·9 mm. at 25° and 328·6 mm. at 35°, as compared with 215·0 and 327·5 mm., respectively, interpolated from Young and Thomas's data. The ester had $d_{4^\circ}^{18^\circ}$ 0·9355 (compare 0·9359, given by the same authors).

Table I gives the total vapour pressures of various ester–water mixtures at 25° and 35°. The normalities refer to 15°, and the pressures are expressed in mm. Hg at 0°. Each figure represents the mean of a number of determinations with different samples of duplicate stock solutions. The variation from this mean was usually of the order ±0·2%, and this probably represents the maximum error in the data. Table II contains the total vapour pressures of ester–sucrose–water mixtures, each of which was 0·2542N with respect to ester. With increasing sucrose content, duplication became less satisfactory, probably owing to increasing difficulty in getting rid of dissolved air as the solutions became more viscous, and the possible error in the data for the highest concentrations of sucrose is about ±0·5%.

From Table II it is seen that the total vapour pressure of a solution which is 0·2542N with respect to ester rises rapidly as the sucrose

TABLE I.

Total Vapour Pressures of Ester–Water Mixtures at 25° and 35°.

Mols. of ester per litre of soln.	Mols. of water per litre of soln.	Total vapour pressure at 25°.	Total vapour pressure at 35°.
0	55·4	23·8	42·2
0·2542	54·5	46·0	80·2
0·5084	53·6	67·2	115·9
1·017	51·6	108·2	176·8
1·525	49·4	144·2	225·1
2·033	47·3	172·2	265·4
Pure ester.	—	214·9	328·6

TABLE II.

Total Vapour Pressures of Ester–Sucrose–Water Mixtures at 25° and 35°.

(Constant concentration of ester = 0·2542 mol./litre.)

G. of sucrose per litre of soln.	Mols. of water per litre of soln.	Total vapour pressure at 25°.	Total vapour pressure at 35°.
0	54·5	46·0	80·2
100	51·0	48·2	83·2
200	47·6	51·4	87·3
300	44·1	55·6	92·8
400	40·7	60·5	99·5
500	37·2	66·7	108·0
600	33·6	75·5	120·8

content increases. This effect is not unexpected in view of the marked displacing effect of the sucrose in solution. This produces a very appreciable increase in the molar fraction of the more volatile component—the ester—with increasing concentration of sucrose.

Partial Vapour Pressures.—These have been determined by the well-known dynamical method. This involves the saturation of a known volume of an indifferent gas with the vapours in equilibrium with the liquid mixture under examination and analysis of the resulting gaseous mixture. In the present work, estimation by a direct absorption method of the amount of each component carried over as vapour is rendered impossible by the fact that the ester vapour would react with any of the reagents normally used for the removal of water vapour. An indirect method of analysis, depending on the combustion of the mixed vapours and subsequent estimation of the products of combustion, was therefore adopted. The same method has been employed by Linebarger (*J. Amer. Chem. Soc.*, 1895, **17**, 615), by Foote and Scholes (*ibid.*, 1911, **33**, 1309), and by Wright (J., 1922, **121**, 2251). The data obtained by Foote and Scholes for the partial vapour pressures of ethyl alcohol and water over alcohol–water mixtures indicate that, with suitable precautions, a fair degree of accuracy can be obtained by this mode of analysis.

Details of the experimental method need not be given. The main features of the technique involve an accurate knowledge of the volume, temperature, and pressure of the air which is to be saturated, and of the pressure of the gas mixture when it leaves the last saturator; the use of an efficient train of saturators; the introduction of an auxiliary oxygen supply beyond the last of these; prevention of condensation of the vapours from the saturated air current; and the usual precautions incidental to combustions.

The partial vapour pressures p_e and p_w of ester and water respectively are given by the relations :

$$p_e = xR\theta(P + p_m - p_s)/132PV,$$
$$p_w = (y - 0{\cdot}4095x)R\theta(P + p_m - p_s)/18PV,$$

where x and y are the weights of carbon dioxide and water resulting from saturation of V litres of dry air measured under atmospheric pressure, P, and at the working temperature θ° Abs., p_m is the working pressure in excess of atmospheric as registered on an auxiliary manometer beyond the last saturator, p_s is the total vapour pressure of the solution, and R is the gas constant expressed in litre-millimetres. In the above equations, the value of p_s already obtained by the static method may be employed, or, alternatively, we need not assume that p_s is known, but substitute $p_s = p_e + p_w$, and solve the two simultaneous equations for p_e and p_w. These methods of calculation lead to substantially the same values of p_e and p_w.

Any experimental error usually affects the value obtained for the partial pressure of water much more than that of ester. The value of p_w is determined by difference between the total water found and the water corresponding to combustion of the ester vapour, and the latter quantity is usually several times greater than the weight of water corresponding to p_w. Hence any error in the estimation of the carbon dioxide (which determines the value of p_e) produces a much greater error in the value of p_w. In the case of the highest concentrations of ester used, an error of 1 mg. in the weight of the carbon dioxide would only affect the value of p_e by 0·1%, but would introduce a 4% error into p_w. The partial pressure of the water might, of course, be obtained indirectly by subtraction of the observed partial pressure of ester from the total vapour pressure of the solution independently obtained.

Tables III and IV contain the results for ester–water and ester–sucrose–water mixtures, respectively, at 25° and 35°. In cols. 2 and 3 of the tables the sum of the observed partial pressures p_e and

p_w is compared with the total vapour pressure p_s obtained by the static method.

TABLE III.

Partial Vapour Pressures of Ester and Water over Ester–Water Mixtures.

Conc. of ester.	p_s.	$p_e + p_w$ (obs.).	p_e. (obs.).	p_e (calc.).	p_w (obs.).	p_w (calc.).
At 25°.						
0·2542	46·0	46·5	22·5	22·3	24·0	23·7
0·5084	67·2	67·8	43·7	43·7	24·1	23·5
1·017	108·2	108·8	85·3	84·9	23·5	23·3
1·525	144·2	144·8	122·0	121·1	22·8	23·1
2·033	172·2	172·5	149·2	149·4	23·3	22·8
At 35°.						
0·2542	80·2	80·4	38·3	38·2	42·1	42·0
0·5084	115·9	115·8	73·9	74·1	41·9	41·8
1·017	176·8	176·4	134·8	135·4	41·6	41·4
1·525	225·1	224·5	183·9	184·2	40·6	40·9
2·033	265·4	267·5	226·6	224·9	40·9	40·5

TABLE IV.

Partial Vapour Pressures of Ester and Water over Ester–Sucrose–Water Mixtures.

(Constant concentration of ester = 0·2542N.)

G. of sucrose per litre of soln.	p_s.	$p_e + p_w$. (obs.).	p_e. (obs.).	p_e. (calc.).	p_w. (obs.).	p_w. (calc.).
At 25°.						
0	46·0	46·5	22·5	22·3	24·0	23·7
100	48·2	48·1	24·6	24·7	23·5	23·5
200	51·4	51·4	28·1	28·1	23·3	23·3
300	55·6	55·5	32·3	32·5	23·2	23·1
At 35°.						
0	80·2	80·4	38·3	38·2	42·1	42·0
100	83·2	82·8	41·3	41·5	41·5	41·7
200	87·3	87·4	45·6	45·9	41·8	41·4
300	92·8	92·2	51·5	51·7	40·7	41·1
400	99·5	99·4	58·6	58·9	40·8	40·6

Discussion of Results.

The values given under p_e (calc.) and p_w (calc.) in Table III are derived as follows. The highest concentration of ester employed is 2·033N, and represents a molar fraction of ester of 0·04117. All the mixtures used are therefore relatively dilute solutions of ester in water and should conform more or less to Raoult's law, *i.e.*, the partial pressure of the solvent water should be approximately equal to the vapour pressure of pure water multiplied by the molar fraction of water in the solution. This gives p_w (calc.), and, subtracting this from the total vapour pressure p_s, the value of p_e (calc.) is obtained.

The general agreement between the observed and the calculated partial pressures in Table III indicates that Raoult's law is valid as a rough approximation for the solvent. It cannot, however, be strictly applicable over the whole range studied, since Henry's law is not obeyed by the solute. The curve obtained by plotting p_e against the molar fraction of ester (N_e) is uniformly concave to the N_e-axis. If we make the probable assumption that very dilute solutions of ester in water obey Raoult's law, it can readily be shown that over the same range of concentration the plot of p_w against N_e is convex to the N_e-axis. This implies that p_w (obs.) should always be greater than p_w (calc.), and that the divergence should be greater the greater the concentration of ester. Our experimental data for p_w (obs.), however, are not sufficiently accurate to afford a test of this point.

Considerable difficulty was experienced in obtaining trustworthy results for ester–sucrose–water mixtures. For solutions of high sucrose content the results were altogether untrustworthy, the partial pressure of ester being abnormally small and that of the water abnormally great. This is just what would be expected if the air current were incompletely saturated with the mixed vapours, and it is probable that the train of saturators used was not efficient enough for the more viscous sucrose solutions. Such data as appear to be trustworthy are in Table IV. As in the case of the ester–water mixtures, the experimental values of the partial pressures are compared with the figures calculated on the assumption that the component water obeys Raoult's law. In estimating the molar fraction of water present, it has been assumed that the sucrose molecule is hydrated by four molecules of water. A fair agreement exists between the observed and the calculated partial pressures. Such agreement is to be expected since (*a*) the concentration of ester is in all cases small, so that, in so far as it affects the partial pressure of the water, Raoult's law should apply as a close approximation; (*b*) the observed vapour pressures of aqueous solutions of sucrose over a considerable range of sucrose content may be calculated fairly accurately from Raoult's law, assuming the above hydration.

Returning to the ester–water case, an interesting point arises when the observed values of p_e at various concentrations of ester are compared at the two temperatures 25° and 35°. The ratio $p_e(35°)/p_e(25°)$ decreases as the concentration or molar fraction of ester increases (see Table V). This means that the latent heat of vaporisation of ester from its aqueous solutions decreases with increasing molar fraction of ester. The same result is obtained if, with a constant concentration of ester, its molar fraction is artificially increased by addition of sucrose. Table VI shows this decrease in the ratio $p_e(35°)/p_e(25°)$ with increasing sucrose content.

TABLE V.

Conc. of ester (mols. per litre).	$p_e(35°)/p_e(25°)$.
0·2542	1·70
0·5084	1·69
1·017	1·58
1·525	1·53
2·033	1·52
Pure ester.	1·53

TABLE VI.

(Constant conc. of ester = 0·2542*N*.)

Conc. of sucrose (g./litre).	$p_e(35°)/p_e(25°)$.
0	1·70
100	1·68
200	1·62
300	1·59

By applying the Duhem–Margules relation to the data of Table V, it readily follows that the ratio $p_w(35°)/p_w(25°)$ *increases* with increasing ester content, which in turn requires that the relative depression of the vapour pressure of the solvent water by addition of ester should be less the higher the temperature. This result is possibly of significance in relation to the evidence recently offered by Kendall and King (J., 1925, **127**, 1778) for the existence of an ester–water complex in aqueous solutions of ethyl acetate. If a similar complex were present in methyl acetate–water mixtures, increase of temperature would certainly favour its dissociation, and the relative depression of vapour pressure of the water would therefore decrease with increasing temperature. In this connexion might also be mentioned the appreciable contraction in volume accompanying the solution of methyl acetate in water.

Summary.

The partial vapour pressures of methyl acetate and water in ester–water and ester–sucrose–water mixtures have been determined at 25° and 35°.

The total vapour pressures of the same systems have been measured by an independent method at these temperatures.

The nature of the partial-pressure curves suggests appreciable compound formation between water and methyl acetate in aqueous solutions of the ester.

One of us (F. P. S.) desires to express his thanks to the Department of Scientific and Industrial Research for a maintenance grant during the course of this work.

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[*Received, October* 16*th,* 1926.]