[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CINCINNATI]

THE ETHYL ACETATE EQUILIBRIUM. II.[1]

BY R. C. CANTELO AND R. D. BILLINGER

RECEIVED JULY 10, 1929 PUBLISHED MARCH 6, 1930

The ethyl acetate equilibrium is represented by the chemical equation $C_2H_5OH + HAc \rightleftharpoons C_2H_5Ac + H_2O$; and the equilibrium constant for the system is given by $K_a = a_3a_4/a_1a_2$ where a_1, a_2, ...are the activities of the ethyl alcohol, acetic acid, ...in the system. In the absence of salts, K_a for this system is considered to be equal to K_E, where $K_E = C_3C_4/C_1C_2$, and C_1, C_2, ...are the molar concentrations.

Poznanski[2] states that Guldberg and Waage's[3] as well as van't Hoff's[4] determinations of the equilibrium constant K_E as calculated from the data of Berthelot and de Saint Gilles for this equilibrium are inaccurate. He states that Schwab[5] found K_E to vary from 1.0 to 6.8. Poznanski found experimentally that if varying quantities of acid are added to a mixture of alcohol and water, K_E varies on both sides of the value 3.79, which he found when 1 mole of acid + 1 mole of alcohol was used as the initial system.

We have throughout our experiments kept the proportions of acid, alcohol and water constant, so that for our purpose, namely, to discover the effect of the addition of salts upon K_E, we are justified in writing $K_a = K_E$ in the *absence* of salts. However, when salts are present, K_E is no longer equal to K_a. K_a is a *true constant* and is related to K_E by the expression $K_a = K_E\Sigma f_{C_2H_5OH}$, where f is the activity coefficient; f for a given species, in the presence of salts, is a function of the ionic strength of the electrolytes present.[6]

In a previous paper[7] we have reported the effects of the salts sodium chloride, sodium iodide and sodium thiocyanate upon the equilibrium constant, K_E, of the ethyl acetate equilibrium. The present communication contains the results which we have obtained by the use of the salts sodium bromide, sodium acetate and sodium nitrite. It includes also the results of our study of the reaction rate constants for this system in the presence of the six salts cited.

---

[1] This paper and a previous one published under the same title represent an abstract of the thesis submitted by R. D. Billinger to the Graduate School of the University of Cincinnati, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Poznanski, *Roczniki Chem.*, **8**, 377 (1928); *C. A.*, **23**, 1559 (1929).

[3] Guldberg and Waage, *J. prakt. Chem.*, **19**, 69 (1879).

[4] Van't Hoff, *Ber.*, **10**, 669 (1877).

[5] Schwab, *Rec. trav. chim.*, **2**, 46 (1883).

[6] Debye and McAuley, *Physik. Z.*, **26**, 22 (1925).

[7] Cantelo and Billinger, THIS JOURNAL, **50**, 3212 (1928).

The general procedure in measuring the values of K_E is given in our first paper. The results obtained with the new series of salts are given in Tables I, II and III; the results for the complete series are shown graphically in Fig. 1. The salt concentration given is the molar concentration in the initial mixture used. The proportions of ethyl alcohol, acetic acid and salt solution were the same as those reported in our previous paper. The temperature was 78°.

TABLE I

EFFECT OF SODIUM BROMIDE

Salt concn.,	Sample	K_E	Av. K_E	Σf
0	A	3.686	3.705	1
0	B	3.725		
0.096	A	4.059	4.068	0.91
	B	4.077		
.191	A	4.094	4.103	.90
	B	4.111		
.289	A	4.254	4.256	.87
	B	4.257		
.382	A	4.461	4.480	.83
	B	4.499		

TABLE II

EFFECT OF SODIUM ACETATE

Concn.	Sample	K_E	Av. K_E	Σf
0.097	A	3.488	3.477	1.07
	B	3.466		
1.90	A	3.556	3.552	1.04
	B	3.547		
.283	A	3.604	3.604	1.03
	B	3.605		
.376	A	3.621	3.652	1.02
	B	3.683		

TABLE III

EFFECT OF SODIUM NITRITE

Concn.	Sample	K_E	Av. K_E	Σf
0.093	A	3.648	3.640	1.02
	B	3.632		
.184	A	3.752	3.710	1.00
	B	3.668		
.279	A	3.829	3.779	0.98
	B	3.729		
.367	A	3.976	3.924	0.95
	B	3.871		

Discussion of Results

The curves in Fig. 1 show how K_E increases with increasing salt concentration. Each salt has its own specific effect; and the salts sodium nitrite and sodium acetate *apparently* depress the equilibrium constant below the value 3.7. It is obvious, however, that in the case of sodium nitrite the reaction $NaNO_2 + HAc \rightleftharpoons KAc + HNO_2$ occurs; and our titration values really give the *total* acid present. We had evidence of the complications arising in the case of this salt in the fact that a considerable pressure developed and a number of filled tubes broke in heating. For this reason the results for this salt must be regarded merely as approximations to the true values.

The variation in K_E due to the presence of dissolved salts arises from the effects of these salts upon the activity coefficients of the reacting species in the equilibrium mixtures. The stoichiometrical concentrations are different in the final mixtures, but the ratio a_3a_4/a_1a_2 is a constant always. Again, even though a_1, a_2. . . . are not always the same in the final mixtures, the above ratio must always be constant, on account of the relation $\bar{\mu}_1 + \bar{\mu}_2 = \bar{\mu}_3 + \bar{\mu}_4$, which holds for chemical equilibrium, where $\bar{\mu}$ is the molecular chemical potential. Any change in a potential of the left-hand member must be accompanied by a compensating change in the right-hand member. The relation between a, the activity, and C, the molar concentration, is given by $a = fC$; f varies with the nature of the thermodynamic environment.

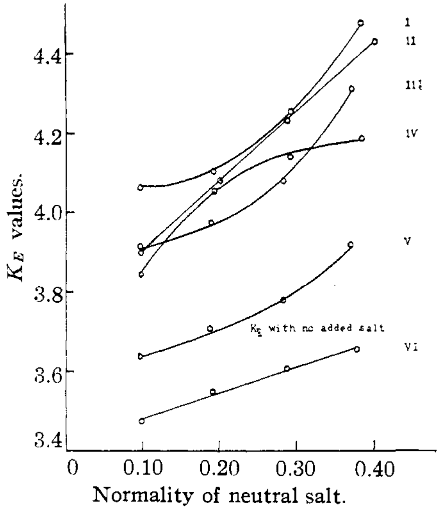

Fig. 1—K_E values: I, NaBr mixtures; II, NaCl; III, NaCNS; IV, NaI; V, $NaNO_2$; VI, $NaC_2H_3O_2$.

Determination of Reaction Velocity Constants.—The velocity of the reaction $C_2H_5OH + HAc \rightleftharpoons C_2H_5Ac + H_2O$ is given by the relation, $V = k'f_1f_2C_1C_2 - k''f_3f_4C_3C_4$, where f and C are the activity coefficient and molar concentration, respectively, at any instant, of a given species, and k' and k'' are constants; f may be expressed as a function of μ, the ionic strength,[6] $\log f = \mu k$, or $f = e^{\mu k}$. Hence, for V we can write

$$V = k'\, e^{\mu(k_1 + k_2)}\, C_1C_2 - k''\, e^{\mu(k_3 + k_4)}\, C_3C_4$$

Unfortunately, we do not know the values of k_1, k_2—, so that we are unable to use the above equation directly for the determination of k' and k''. We are forced, therefore, to use the classical expression for V, namely

$$V = k_1C_1C_2 - k_2C_3C_4$$

and to calculate k_1 and k_2 solely by an application of mathematics, and then to attempt a determination of the true values of k' and k''.

For the reaction $C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$, let a, b, c and d denote the initial concentrations in moles per liter of alcohol, acid, ester and water, and let the amount of change after the time t be x. The velocities of the direct and reverse reactions are

$$\frac{dx_1}{dt} = k_1(a - x)\,(b - x),\ \frac{dx_2}{dt} = k_2\,(c + x)\,(d + x)$$

hence the velocity of esterification is

$$\frac{dx}{dt} = k_1(a - x)(b - x) - k_2\,(c + x)\,(d + x)$$

This equation may be integrated, giving, finally, the expression

$$k_2 = \frac{1}{t} \cdot \frac{K-1}{P} \log \frac{(Q-P)[Q+P-2(K-1)\,x]}{(Q+P)[Q-P-2(K-1)\,x]}$$

where K is the equilibrium constant, defined by $K = k_1/k_2$

$$P = \sqrt{Q^2 - 4(K-1)\,(Kab - cd)} \text{ and } Q = [K(a+b) + (c+d)]$$

Experimental Method

The general procedure was similar to that described under the determination of K_E. Since the reaction rate is slow at room temperature, the actual starting time was not taken until the mixtures were sealed in tubes and the tubes immersed in boiling carbon tetrachloride. The time of stopping was taken when the tubes were withdrawn from the heating flask and immersed in ice water, prior to titration of the acetic acid present. Thus the time recorded in the tables represents the time during which the samples were at the temperature of boiling carbon tetrachloride.

The proportions of ethyl alcohol, acetic acid and salt solution in the initial mixture were the same as in the equilibrium experiments.

The values of k_2 for the reaction were calculated from the data obtained by the use of the equation given above. For K in that equation we substituted the determined value K_E for the salt concentration used. However, the ratio k_1/k_2 is probably not constant, so that the values given in Table V are the averages of the *last three measurements* only. In Table IV, however, we give complete values for two series, in order to show the trend of the values of k_2. We found this trend in all our series.

TABLE IV

REACTION VELOCITY CONSTANTS IN PRESENCE OF 0.200 N SODIUM CHLORIDE AND OF 0.298 N SODIUM THIOCYANATE

0.2 N Sodium chloride		0.3 N Sodium thiocyanate	
Time, minutes	k_2	Time, minutes	k_2
73	0.000261	98	0.000181
138	.000228	137	.000119
198	.000222	174	.000116
230	.000221	263	.000113
288	.000215	297	.000105
408	.000186	329	.000108

TABLE V

THE EFFECT OF VARIOUS SALTS UPON THE VELOCITY CONSTANT k_1 (TEMP., 78°)

$k_1 \cdot 10^4 = k_2$.detd. $K_E \cdot 10^4$

Salt concn.	NaCl	NaCNS	NaI	NaBr	NaAc	$NaNO_2$
0.1	6.16	4.25	5.23	6.58	0.643	0.668
.2	8.46	4.43	5.75	8.39	.671	.529
.3	10.06	4.41	6.83	10.83	.623	.753
.4	10.90	5.20	5.83	12.75	.623	.531

0.00 salt gave $k_1 \times 10^4 = 3.86$. 0.02 HCl gave $k_1 \times 10^4 = 29.19$.

The results are shown graphically in Fig. 2.

Discussion of Results

The effects of the anions in increasing the reaction velocity seem to be almost in the same order as that indicated in the displacement of equilibrium, except that here the iodide seems to have a greater effect than the thiocyanate ion.

The explanation of the cause of the increased velocities, that is, the catalytic effect, might be attempted in terms of various theories. These theories may be summarized briefly as follows: (1) increased hydrogen-ion concentration,[8] (2) hydration of salt with resulting increase in hydrogen-ion concentration[9] (Manning's work,[10] however, seems to show that hydration of solute does not affect the reaction rate constants), (3) increased activity of hydrogen ion,[11] and of hydrogen ion and of the undissociated molecule,[12] (4) shift in the water equilibrium;[13] this amounts to a change in solvent, in which concentrations, reaction velocities, ionization, etc., will be different from those in the original solvent, (5) the activity theory of reaction rate,[14] (6) Brönsted's theory of reaction velocity,[15] (7) change in the thermodynamic potential caused by a change in the field surrounding the reacting substances.[16]

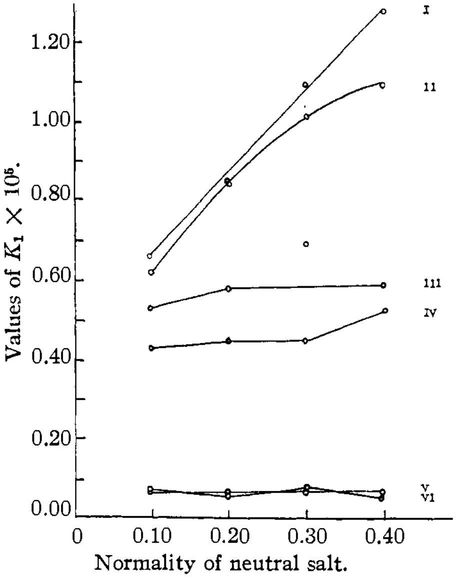

Fig. 2.—Reaction rate curves: I, NaBr mixtures; II, NaCl; III, NaI; IV, NaCNS; V, $NaC_2H_3O_2$; VI, $NaNO_2$.

This last is substantially the hypothesis we have used in our investigation. We believe that the effect of salts upon equilibrium and velocity constants is due to changes in the activity coefficients of the reacting substances. This change itself is due to the new thermodynamic environment of the reacting substances in the presence of salts.

---

[8] Arrhenius, *Z. physik. Chem.*, **31**, 197 (1899); Euler, *ibid.*, **32**, 348 (1900).

[9] Wilson, This Journal, **42**, 715 (1920).

[10] Manning, *J. Chem. Soc.*, **119**, 2079 (1921).

[11] Åkerlöf, *Z. physik. Chem.*, **98**, 260 (1921).

[12] Taylor, This Journal, **37**, 551 (1915).

[13] Bancroft, *J. Phys. Chem.*, **30**, 1194 (1926); Bowe, *ibid.*, **31**, 291 (1927).

[14] Harned and Seltz, This Journal, **44**, 1476 (1922).

[15] Brönsted, *Z. physik. Chem.*, **102**, 169 (1922).

[16] Acree, This Journal, **41**, 474 (1919).

Most other investigators of the influence of salts upon rates of esterification have used hydrochloric acid as well; and the increased velocity has been attributed to the increase in hydrogen-ion concentrations. Our investigations were carried out in the absence of mineral acid, so that if the presence of salts varied the hydrogen-ion concentration or activity, it was the hydrogen-ion concentration or activity resulting from the reaction mixture—acetic acid, ethyl alcohol and water.

Using our determined values for k_1 and k_2, we may write

$$V = k_1C_AC_B - k_2C_EC_F \tag{1}$$

and also we may write

$$V = k'C_AC_Bf_Af_B - k''C_EC_Ff_Ef_F$$

Then equating coefficients of like terms, we have

$$k_1 = k'f_Af_B;\ \ k_2 = k''f_Ef_F \text{ or}$$
$$\log k_1 = \log k' + \log f_A + \log f_B, \text{ etc.}$$

If we assume that the Debye–McAuley relation holds for this system, we have

$$\log k_1 = \log k' + \mu k_A + \mu k_B$$
$$\log k_1 = \log k' + m\mu$$

where m is a constant.

We may test this relation by plotting $\log k_1 + 5$ against μ, which is here equal to C, the molar salt concentration. Such a plot is given in Fig. 3. Omitting entirely the plot for sodium nitrite, it is seen that the points fall approximately upon straight lines. While the points for sodium acetate fall very well upon a straight line, yet this line does not tend toward the same $\log k_1$ value for zero concentration as do the others. It is evident that a secondary salt effect has come into play in this case.

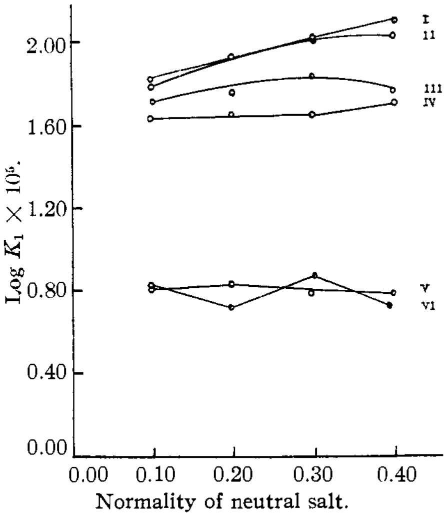

Fig. 3.—I, NaBr mixtures; II, NaCl; III, NaI; IV, NaCNS; V, $NaC_2H_3O_2$; VI, $NaNO_2$.

Extrapolation to zero concentration of added salt gave the following values

For sodium bromide, 0.000537
For sodium chloride, 0.000457
For sodium iodide, 0.000467
For sodium thiocyanate, 0.000437

These values are somewhat higher than the value 0.000386 obtained for k' in the absence of salts.

We hope to continue the investigation in the region 0.10 to zero ionic strength of the four salts mentioned above, and also to extend the study to salts of higher valence type. At the same time we are planning a study of the effect of the six salts upon the activity of the hydrogen ion of water and of acetic acid.

Summary

The relation between the true equilibrium constant, K_a, for the ethyl acetate equilibrium in the presence of salts, and the constant K_E calculated from the classical mass action expression is $K_a = K_E \Sigma f_1$, where f is the activation of a given reacting species. The term Σf varies with the salt present, giving rise to different values of K_E.

The value of K_E has been determined in the presence of the salts sodium bromide, sodium acetate and sodium nitrite. The values for sodium nitrite as added salt are considered to be only approximate. The value of K_E increases with the concentration of added salt. With sodium acetate as added salt, K_E is less than the value obtained in the absence of salts, and K_E increases linearly with the concentration of sodium acetate.

The velocity constants for the reaction have been determined by means of an expression which contains K_E, the determined equilibrium constant for the specific salt, and specific concentration. Values are reported for the specific reaction rates for the forward action for six salts. The values reported are those in the neighborhood of equilibrium where $K_E = k_1/k_2$.

The order of the effects of the salts upon the velocity of reaction is almost the same as that indicated in the displacement of equilibrium. The specific reaction rate is practically constant for all concentrations of sodium acetate. A secondary salt effect evidently occurs with sodium acetate, so that its effect cannot be interpreted in the same way as can the effects of the salts sodium iodide, bromide, chloride and thiocyanate.

The Debye–McAuley relation for the activity of non-electrolytes has been used to obtain an equation for the rate of the esterification reaction. This equation has been combined with the classical expression to obtain a relation to test the validity of the former equation. It has been shown that this equation is in substantial agreement with the experimental data.

CINCINNATI, OHIO