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

THE ETHYL ACETATE EQUILIBRIUM

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When the system ethyl alcohol, acetic acid, ethyl acetate and water has reached a state of equilibrium for a given temperature and pressure, this equilibrium state is expressed by the chemical equation $C_2H_5OH + HAc \rightleftharpoons C_2H_5Ac + H_2O$.

For a virtual change from equilibrium $dZ = O$, where Z is the thermodynamic potential, and since $dZ = \Sigma\mu dm$, where μ = specific chemical potential and m = mass of component, we may write: $\bar{\mu}_1 + \bar{\mu}_2 = \bar{\mu}_3 + \bar{\mu}_4$, where $\bar{\mu}_1$, $\bar{\mu}_2$, - - - are the molecular chemical potentials respectively of ethyl alcohol, acetic acid, - - -.

Now for each of the four substances constituting the system we have an equation of the form $\bar{\mu}_1 - \bar{\mu}_{1,0} = RT \ln a_1$, where a_1 is the thermodynamic concentration or activity of the component in the system, $a_{1,0}$ for the standard state being arbitrarily placed equal to 1. It is then a simple matter to derive the mass action expression for equilibrium, namely, $K_a = a_3a_4/a_1a_2$. Now it is quite possible that a change in the thermodynamic environment may change the value of one or more of the chemical potentials of the substances involved, and such changes in chemical potential will result in a change in the value of K_a, the equilibrium constant.

In the present investigation we have sought to change the thermodynamic environment by using in place of water alone solutions of the salts sodium chloride, sodium thiocyanate and sodium iodide. These salts form a Hofmeister series as follows: $\overline{CNS}$ $\overline{I}$ $\overline{Cl}$, as regards their relative effects in retarding gelation, that is, in lowering the temperature of gelation. The relative effects of these salts are of interest, therefore, with respect to the water equilibrium. Bancroft[1] considers liquid water to be an equilibrium mixture of hydrol and polyhydrol, the latter being a polymerized form of the former. He ascribes the greater peptizing action of potassium iodide over potassium chloride on gelation in water to the water equilibrium being shifted in the direction of more hydrol, the peptizing agent.

Schlesinger[2] investigated the influence of $LiCl$, $NaCl$, KCl and $CaCl_2$ on the ethyl acetate equilibrium at 100°, and found that the equilibrium was shifted, owing to the presence of these salts. He found that with $NaCl$, $LiCl$ and $CaCl_2$, his equilibrium constant could be calculated from the linear equation, $K = 3045 - 21.217\ C$, C being the salt concentration in milliequivalents per mole of water.

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[1] Bancroft, *J. Phys. Chem.*, **30**, 1194 (1926).

[2] Schlesinger, *Ber.*, **59B**, 1965 (1926).

Experimental Method

Weighed quantities of acetic acid, ethyl alcohol and water or salt solution were mixed together in a weighed flask. From this mixture small glass tubes were filled and sealed by means of a blast lamp. The tubes were weighed before and after filling to obtain the weight of sample taken.

The method of filling the tubes was to fit up the weighed flask as a wash bottle with a capillary jet; then by means of current of air, dried by passing through calcium chloride, it was possible to force the liquid into the small tubes.

The acetic acid, ethyl alcohol and neutral salts used were all C. P. chemicals which were tested for impurities. The acid contained 99.39% of acetic acid by weight and the alcohol 95.75% by weight. The salts were all thoroughly dried before using.

The sealed tubes were placed in a bath of carbon tetrachloride which was kept refluxing by a simple heater. The heater consisted of a 100-watt incandescent lamp in a can insulated with sheet asbestos. By this arrangement it was possible to keep the tubes containing the esterification mixture at a temperature of 78°.

Esterification in the absence of a mineral acid catalyst is slow, even at this temperature, and it was necessary to continue the heating for from thirty to forty days. Then from time to time a tube was taken from the bath, cooled in ice, the capillary end broken and the contents placed in ice cold, freshly boiled water. The mixture was transferred to a volumetric flask and an aliquot portion taken for titration against standard barium hydroxide solution. By means of the titration value the concentration of acetic acid was known in the resulting mixture, and from the known initial concentrations it was possible to calculate the concentration of all four constituents in the equilibrium mixture. Concentrations were figured in terms of millimoles of the constituents and the equilibrium constant K_E was then expressed as

$$K_E = \frac{\text{Millimoles of } CH_3COOC_2H_5 \times \text{Millimoles of } H_2O}{\text{Millimoles of } CH_3COOH \times \text{Millimoles of } C_2H_5OH}$$

When several successive samples gave approximately equal values of K_E, the equilibrium was assumed to have been reached.

Table I

Esterification with No Added Salt

Run	Sample	K_E	Av. K_E	Concn., init.	CH_3-COOH final	Concn. init.	C_2H_5OH, final	Concn. init.	H_2O, final	Concn. CH_3-$COOC_2H_5$, final
1st	A	3.686	3.705	866.9	459.8	848.4	441.3	1430.4	1837.5	407.1
	B	3.723		866.9	458.6	848.4	439.7	1430.4	1838.7	408.3
2nd	A	3.755	3.708	867.8	458.4	847.6	438.2	1433.0	1842.4	409.4
	B	3.661		867.8	461.5	847.6	441.3	1433.0	1839.3	406.3

The initial concentration refers to the concentration, expressed in millimoles, in the original mixture before reaction occurs. The final concentration refers to the concentration after equilibrium is established.

TABLE II

ESTERIFICATION IN THE PRESENCE OF SODIUM CHLORIDE

Neutral salt, *N*	Sample	K_E	Av. K_E	Concn. init.	CH_3-COOH final	Concn. init.	C_2H_5OH, final	Concn., init.	H_2O, final	Concn. CH_3-$COOC_2H_5$, final
0.481	A	3.872	3.902	170.9	91.55	163.4	84.0	296.2	375.5	79.3
	B	3.931		170.9	91.06	163.4	83.5	296.2	376.0	79.8
1.000	A	4.089	4.082	865.3	444.7	848.4	427.8	1429.2	1849.8	420.6
	B	4.074		865.3	445.2	848.4	428.3	1429.2	1849.3	420.1
1.426	A	4.221	4.235	866.7	443.5	857.7	434.5	1499.0	1922.2	423.2
	B	4.249		866.7	442.6	857.7	433.6	1499.0	1923.1	424.1
2.000	A	4.413	4.438	866.8	435.4	848.8	417.5	1428.7	1860.0	431.3
	B	4.463		866.8	433.9	848.8	416.0	1428.7	1861.5	432.8

TABLE III

ESTERIFICATION IN THE PRESENCE OF SODIUM IODIDE

Neutral salt, *N*	Sample	K_E	Av. K_E	Concn. init.	CH_3-COOH final	Concn. init.	C_2H_5OH, final	Concn., init.	H_2O, final	Concn. CH_3-$COOC_2H_5$, final
0.477	A	3.839	3.848	170.9	91.29	163.6	83.99	290.2	369.81	79.61
	B	3.857		170.9	91.16	163.6	83.86	290.2	369.94	79.74
0.946	A	4.053	4.056	170.9	90.31	163.6	83.01	296.5	377.09	80.59
	B	4.059		170.9	90.27	163.6	82.97	296.5	377.13	80.63
1.448	A	4.128	4.143	170.8	89.39	163.2	81.79	289.3	370.71	81.41
	B	4.159		170.8	89.25	163.2	81.65	289.3	370.85	81.55
1.902	A	4.192	4.186	170.5	89.09	162.8	81.39	292.0	373.41	81.41
	B	4.179		170.5	89.17	162.8	81.47	292.0	373.33	81.33

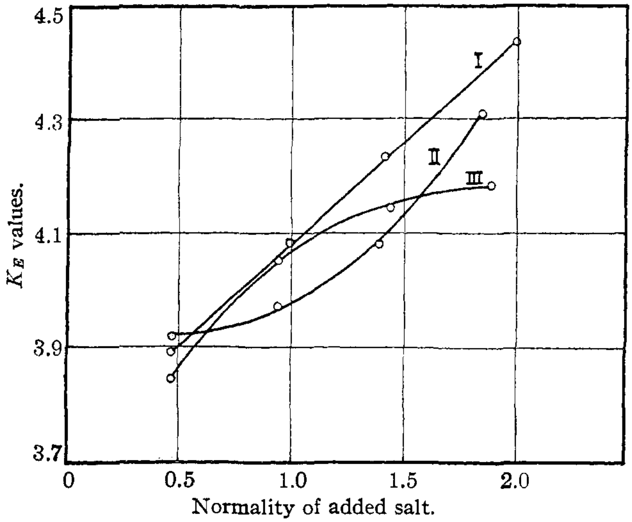
TABLE IV

ESTERIFICATION IN THE PRESENCE OF SODIUM THIOCYANATE

Neutral salt, *N*	Sample	K_E	Av. K_E	Concn. init.	CH_3-COOH, final	Concn., init.	C_2H_5OH, final	Concn., init.	H_2O, final	Concn. CH_3-$COOC_2H_5$, final
0.473	A	3.893	3.916	170.9	91.49	163.1	83.69	295.7	375.11	79.41
	B	3.939		170.9	91.15	163.1	83.35	295.7	375.45	79.75
0.938	A	3.927	3.973	171.8	91.54	163.3	83.04	291.7	371.96	80.26
	B	4.018		171.8	90.94	163.3	82.44	291.7	372.56	80.86
1.407	A	4.114	4.080	171.3	90.24	163.2	82.14	295.2	376.26	81.06
	B	4.046		171.3	90.68	163.2	82.58	295.2	375.82	80.62
1.840	A	4.319	4.313	170.6	88.33	163.8	81.53	295.8	378.07	82.27
	B	4.307		170.6	88.40	163.8	81.60	295.8	378.00	82.20

Discussion of Results

Tables II, III and IV, and Fig. 1 show that K_E increases with increasing salt concentrations. When sodium chloride is the added salt, the equilibrium constant is a linear function of the concentration of the salt, but the effect of sodium iodide and sodium thiocyanate is more complicated. Each salt appears to have its own specific effect and work at present in progress in this Laboratory seems to indicate that one salt at least depresses the equilibrium constant below the value 3.7. Further work is evidently necessary before our values may be explained, and work is now in progress with a view to determining the relative chemical potentials of the components in the system with and without the addition of salts. It may be pointed out, however, that the Hofmeister series does not appear to hold for the order of the effects upon the equilibrium constant at 78°.



I, Curve for K_E values with NaCl; II, curve for K_E values with NaCNS; III, curve for K_E values with NaI.

Fig. 1.

Summary

The ethyl acetate equilibrium depends upon the equality of the sum of the chemical potentials of the ethyl alcohol and acetic acid to the sum of the chemical potentials of the ethyl acetate and water. Any change in thermodynamic environment may change the value of one or more of these potentials, thereby giving a new value for the equilibrium constant.

The equilibrium constant in the absence of salts for this system has been measured and found to be equal to 3.7.

The equilibrium constant in the presence of salts has been measured and found to increase with the concentration of the salt in the water solution used in place of water alone. With sodium chloride as added salt, the equilibrium constant increases linearly with the concentration of sodium chloride. With sodium thiocyanate and sodium iodide, the effect is more complicated.

The order of the effects of the anions upon the equilibrium constant is not that of a Hofmeister series.

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