THE EFFECT OF TEMPERATURE ON THE MOLECULAR SURFACE ENERGY OF BINARY MIXTURES. II. WATER AND NICOTINE

BY W. F. SEYER AND A. F. GALLAUGHER

A previous communication[1] embodied the results of surface tension measurements carried out upon mixtures of a polar and non-polar liquid, sulfur dioxide and benzene. The following pages contain the results of similar measurements made on mixtures of two polar liquids, water and nicotine. The investigation had a two-fold object: to find the effect of temperature on the molecular surface energy of a binary mixture of two polar liquids both of which would ordinarily be assumed to be associated, and to find further evidence to support the theory of hydrate formation in the case of nicotine and water.

Nicotine dissolves in its own volume of water to form a sticky, viscous liquid, which on warming becomes turbid and separates into two liquid layers, the upper being a saturated solution of nicotine in water, and the lower a saturated solution of water in nicotine. Further warming will again
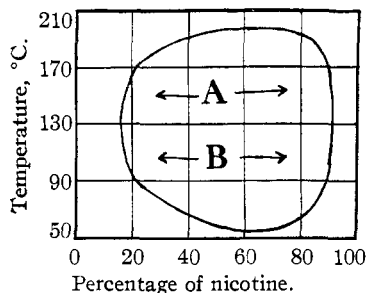

Fig. 1.

bring about the formation of a single homogeneous phase. Ever since the discovery of the ring-shaped solubility curve of nicotine and water by Hudson,[2] attempts have been made to show the existence of hydrates at the temperatures below the lower critical temperature, hoping thereby to explain this peculiar phenomenon. The upper portion of the curve in Fig. 1, above the line AB, is similar in shape to that obtained whenever any two immiscible liquids are heated. In such cases complete miscibility occurs whenever the kinetic energy of the molecules of the liquids is sufficient to overcome the internal pressures. Solution in this case is obviously only a matter of diffusion. The portion of the curve below AB which defines the limits of complete miscibility has been quite generally ascribed to the existence of hydrates. These hydrates act in bringing about solution in a manner similar to that of alcohol when added to a two-phase ether–water system. If the temperature of a homogeneous solution containing equal amounts of water and nicotine is then raised to 61°, these supposed hydrates are decomposed and, as a consequence, the two phases make their appearance.

Considerable work has been done with the object of establishing the

[1] Seyer and Peck, THIS JOURNAL, **51**, 14 (1929).

[2] Hudson, *Z. physik. Chem.*, **47**, 113–115 (1904).

existence of these hydrates. Owing to the viscous nature of the solutions at temperatures below 20°, it has so far been difficult to obtain reliable freezing point data and quite impossible to separate any hydrates which might have been formed. While Jephcott[3] upon an examination of the freezing points of solutions of nicotine found indications of hydrates, still, most of the evidence supporting the theory of hydrate formation has come from the investigation of other physical properties of nicotine and water solutions. Thus Tsakalotos[4] investigated the viscosity, Skalweit[5] the specific gravity, Winther[6] the index of refraction and specific rotatory
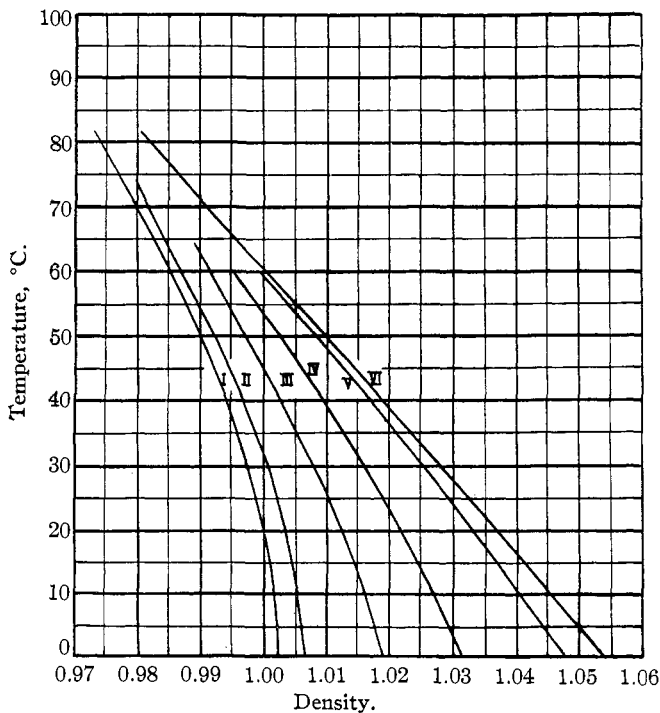

Fig. 2.

power, all with a view toward offering an explanation of the closed solubility curve. Tsakalotos found the viscosity of various mixtures to be much greater than that calculated from the rule of mixtures, the curve for the coefficient of viscosity of the system showing a well-defined maximum at 78% concentration of nicotine. Skalweit observed that when water is added to nicotine, heat is produced and a diminution of volume takes place, and that the densities of the mixtures show a maximum at 72% nicotine

[3] Jephcott, *J. Chem. Soc.*, **115**, 104 (1919).

[4] Tsakalotos, *Bull. soc. chim.*, [4] **5**, 397 (1909).

[5] Skalweit, *Ber.*, **14**, 1809–1810 (1881).

[6] Winther, *Z. physik. Chem.*, **60**, 563 (1907).

concentration. Jephcott points out that if the density or specific rotatory power of nicotine in aqueous solutions is plotted against concentration, a series of maxima is obtained. He also observed that the time required for equilibrium to be established at 40 and 80% nicotine was appreciable. The results of these various investigations seem to show the possibilities of hydrate formation at concentrations of about 40 and 80% nicotine. As will be shown later, the surface tension measurements of the solutions at different temperatures also support this view.
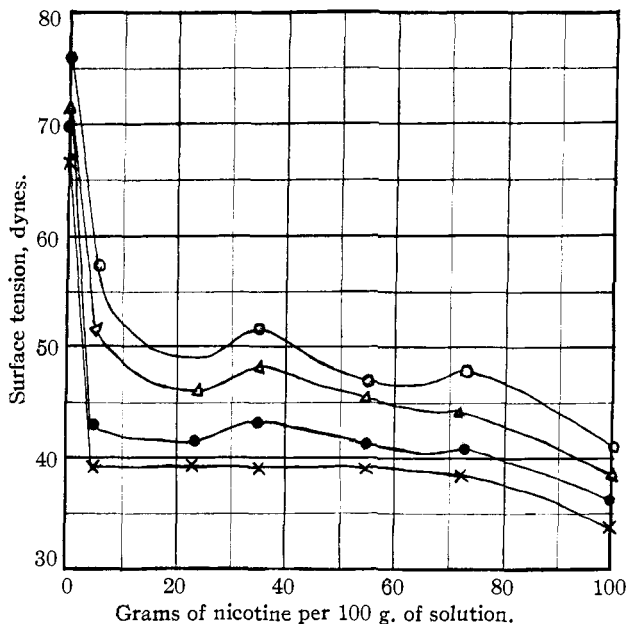

Fig. 3.—○, Curve for 0°; △, curve for 20°; ●, curve for 40°; ✕, curve for 60°.

Determinations of Densities and Surface Tensions.—The method used for determining the densities of nicotine and its aqueous solutions was the same as that used for benzene and sulfur dioxide solutions below −10°.

This required finding the loss in weight of a quartz sinker when weighed in the liquid.[1] The apparatus and technique involved in the surface tension measurements were also the same as formerly described. The readings were always made with a falling meniscus and in most cases a much longer time was required for the nicotine–water solutions to reach equilibrium than was the case with benzene–sulfur dioxide solutions, which was to be expected in view of the greater viscosities of the former solutions. In most cases it required from five to six hours before the readings became constant.

Preparation of Materials.—The nicotine was obtained from the Eastman Kodak Co. and had a boiling point of 115–117° at 12-mm. pressure.

As it could not be purified by recrystallization, it was redistilled several times under vacuum, the first and last portions of the distillates being rejected.   In this way a fraction was obtained which distilled within one degree at 12-mm. pressure.   To prevent oxidation the purified nicotine was kept in bottles that were completely filled as suggested by Jephcott, with the result that no coloration was discernible even after standing for several months.   The water used in preparing the aqueous solutions was of the purity required for conductivity work.   From these materials six solutions were prepared and kept in containers free from air until ready for use. The composition of the solutions is given in Table I.

TABLE I

COMPOSITION OF MIXTURES

Mixture	I	II	III	IV	V	VI
Nicotine/100 g. of soln., g.	5.35	10.12	23.74	35.15	54.86	72.16
Average molecular weight	18.91	...	23.55	26.13	35.08	50.17

The following series of tables contains the densities of nicotine and of nicotine–water solutions at different temperatures corrected to vacuum.

TABLE II.   NICOTINE

Temp., °C.	Density[a]
−49.18	1.0616
−41.03	1.0556
−30.23	1.0473
−19.27	1.0385
−10.45	1.0318
− 0.85	1.0241
9.58	1.0159
19.27	1.0081
30.18	1.0001
49.49	0.9850
59.98	.9765
76.93	.9631
97.64	.9465
118.22	.9297
138.91	.9131
163.92	.8923
183.18	.8763
208.28	.8495

TABLE III.   MIXTURE I

Temp., °C.	Density
3.10	1.0027
10.20	1.0024
20.20	1.0002
29.90	0.9975
40.10	.9939
51.20	.9894
60.50	.9847
70.80	.9793
75.40	.9768
79.60	.9741

TABLE IV.   MIXTURE II

Temp., °C.	Density
1.0	1.0070
10.27	1.0058
19.80	1.0036
30.70	1.0003
40.30	0.9967
50.60	.9919
59.70	.9873
69.80	.9817

TABLE VI.   MIXTURE IV

Temp., °C.	Density
1.05	1.0313
10.20	1.0268
20.00	1.0216
30.40	1.0156
39.80	1.0095
50.30	1.0026
60.45	0.9951

TABLE V.   MIXTURE III

Temp., °C.	Density
0.40	1.0193
10.30	1.0163
19.90	1.0127
29.30	1.0082
40.20	1.0031
50.60	0.9970
61.40	.9905

TABLE VIII.   MIXTURE VI

Temp., °C.	Density
1.00	1.0534
9.80	1.0462
19.40	1.0376
30.10	1.0280
40.10	1.0191
50.10	1.0100
60.20	1.0006
70.00	0.9914
75.90	.9856

TABLE VII.   MIXTURE V

Temp., °C.	Density
0.40	1.0474
10.20	1.0403
20.00	1.0330
29.80	1.0252
40.20	1.0167
50.40	1.0079
62.7	0.9974

[a] Densities corrected to vacuum.

Figure 1 shows that with increasing nicotine concentration the temperature–density relationships become almost linear. The densities of the nicotine vary somewhat from those previously recorded, which is what might be expected in view of the great difficulty encountered in purifying nicotine.

The surface tension values were calculated by means of the formula $\gamma = KHd$ where γ is the surface tension in dynes, K a constant for the apparatus employed, H the corrected difference in height of liquid in the two capillaries and d the density of the solutions. Two surface tension tubes were
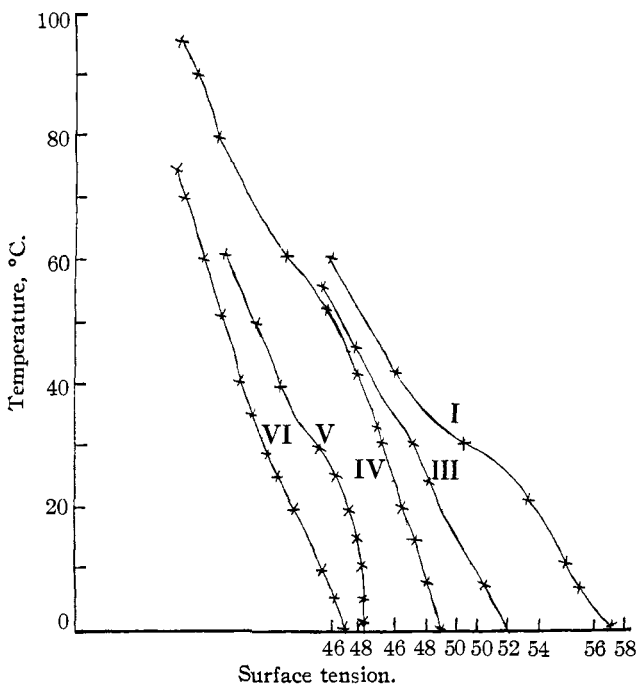

Surface tension.

Fig. 4.

employed whose constants were 15.026 and 18.482. In the case of the solutions so far examined the density of the vapor was so small as to be negligible. Since the surface tensions were determined at slightly different temperatures from that of the densities, it was necessary to interpolate to get the required densities, for the surface tension calculations. The Eötvös constant in the case of nicotine was obtained by plotting the molecular surface energies against temperatures on a large scale and then taking the differences of the molecular surface energies from the curves over intervals of about 30°. The total surface energies for certain temperatures have been calculated as well as the constant C in Macleod's[7] equation

[7] Macleod, *Trans. Faraday Soc.*, **29**, 38 (1923–1924).

$\gamma = C(D - d)^4$ where γ is the surface tension, D the densities of the liquid and d the density of the vapor, from the surface tension directly.   The surface tension and the other derived quantities are given in their accustomed units in the following tables.

TABLE IX

SURFACE TENSION AND OTHER DATA

Temp., °C.	Density	h corr.	Surface tension, dynes/ cm.	Mol. surface energy, ergs/ sq. cm.	Eötvös constant, K_c	Total surface energy, ergs/ sq. cm.	Macleod constant, C
−49.31	1.0627	2.37	46.58	1331		71.0	36.78
−39.55	1.0546	2.34	45.39	1307			37.00
−28.95	1.0465	2.29	44.12	1277			36.98
−19.09	1.0392	2.25	43.16	1244	2.5	70.0	37.86
− 9.19	1.0305	2.22	42.22	1227			37.78
0.75	1.0230	2.18	41.41	1206			37.78
11.41	1.0147	2.13	39.89	1174	2.6	69.9	37.61
20.55	1.0072	2.08	38.61	1141			37.52
30.19	1.0000	2.04	37.70	1121			37.70
39.83	0.9915	1.99	36.54	1092	2.7	70.9	37.77
51.01	.9837	1.94	35.37	1063			37.76
60.66	.9760	1.89	34.15	1032			37.64
70.86	.9665	1.85	33.08	1005	2.8	70.7	37.86
79.06	.9607	1.81	32.17	983			37.77
89.07	.9527	1.77	31.25	959			37.63
93.45	.9490	1.76	30.99	953	2.4	67.0	38.01

TABLE X

MIXTURE I

Temp., °C.	Density	h corr.	Surface tension, dynes/cm.	Mol. surface energy, ergs/sq. cm.	Eötvös constant, K_c
0.09	1.0029	3.79	57.13	404.6	
6.20	1.0025	3.66	55.25	391.8	1.6
10.30	1.0021	3.61	54.39	385.5	
20.80	1.0003	3.46	52.14	370.0	
29.70	0.9978	3.19	47.91	340.0	2.2
41.50	.9940	2.92	43.65	326.6	
52.10	.9893	2.81	41.85	299.1	
60.53	.9845	2.63	38.94	279.3	1.1
70.30	.9793	2.52	37.11	267.1	
79.97	.9740	2.38	34.84	252.8	
90.27	.9685	2.30	33.54	243.2	1.3
95.40	.9685	2.22	32.30	234.6	

MIXTURE III

0.41	1.0192	2.59	48.83	396.3	
7.82	1.0172	2.55	48.12	390.8	
14.85	1.0147	2.51	47.23	384.4	0.8
19.67	1.0129	2.47	46.41	378.5	
25.27	1.0104	2.46	46.06	375.9	
30.46	1.0080	2.43	45.31	370.3	

TABLE X   (*Concluded*)

Temp., °C.	Density	h corr.	Surface tension, dynes/cm.	Mol. surface energy, ergs/sq. cm.	Eötvös constant, Kc
35.60	1.0056	2.40	44.73	365.5	
44.92	1.0007	2.31	42.88	350.8	1.5
60.00	0.9953	2.14	39.52	325.1	

TABLE XI

MIXTURE IV

Temp., °C.	Density	h corr.	Surface tension, dynes/cm.	Mol. surface energy, ergs/sq. cm.	Eötvös const., Kc
0.24	1.0314	2.70	51.55	444.5	
7.70	1.0284	2.64	50.34	435.5	
19.90	1.0223	2.51	47.54	412.7	1.4
24.80	1.0195	2.48	46.73	407.4	
30.56	1.0157	2.43	45.68	399.2	
35.30	1.0130	2.39	44.92	392.1	1.8
46.20	1.0055	2.26	42.13	369.5	
55.86	0.9982	2.17	40.06	353.4	

TABLE XII

MIXTURE V

Temp., °C.	Density	h corr.	Surface tension, dynes/cm.	Mol. surface energy, ergs/sq. cm.	Eötvös constant, Kc
1.88	1.0467	2.41	46.77	525.2	
11.17	1.0403	2.43	46.85	527.5	
15.50	1.0370	2.42	46.48	523.7	0.8
19.75	1.0335	2.40	45.99	520.6	
25.62	1.0291	2.36	45.00	508.2	
29.75	1.0257	2.32	44.00	500.9	
34.76	1.0218	2.23	42.13	480.8	
39.55	1.0172	2.19	41.35	473.0	1.9
51.20	1.0070	2.12	39.62	456.4	
61.20	0.9985	2.05	37.96	470.2	

TABLE XIII

MIXTURE VI

Temp., °C.	Density	h corr.	Surface tension, dynes/cm.	Mol. surface energy, ergs/sq. cm.	Eötvös constant, Kc
0.42	1.0540	2.43	47.37	622.3	
5.50	1.0500	2.40	46.75	615.2	
10.20	1.0462	2.37	45.88	605.7	1.8
19.85	1.0374	2.31	44.29	587.5	
25.02	1.0327	2.27	43.30	576.8	
29.17	1.0288	2.24	42.65	570.6	1.6
34.97	1.0236	2.20	41.77	560.4	
40.30	1.0185	2.17	40.90	548.8	
50.45	1.0091	2.12	39.67	536.5	
60.00	1.0002	2.08	38.49	523.6	1.4
69.65	0.9914	2.02	37.10	507.6	
75.05	.9862	2.00	36.58	502.3	

The values of the Eötvös constant for nicotine are larger than the theoretical, 2.12.   Using the empirical equation of Walden and Swinne,[8] $K_c = 1.90 + 0.011\ (\Sigma NA)$ where (ΣNA) represents the sum of the square roots of the atomic weights of the elements in the compound, a value of K_c is obtained which is numerically equal to 2.50, about the average of the value found experimentally.   There appears to be a gradual increase in this value with temperature up to about 75° and then a falling off.   Whether this decline would continue until the theoretical value is reached will be discussed in a further communication.   In any case there seems to be no basis for considering the nicotine associated.   This is further borne out by the consistent values of the Macleod constant and by the values of the Hildebrand[9] functions for nicotine.   The values are as follows: $\gamma/V^{1/3} = 7.65$, $E_\sigma/V^{1/3} = 14.1$, in which γ is the surface tension, V the molal volume and E_σ the total surface energy.   It is thus seen that nicotine has an internal pressure about equal to that of thiophene and bromobenzene.

If the surface tension values of the solution are plotted against temperature, the curves obtained all show a deviation from a straight line.   It would appear from the curves that between 15 and 35° alterations in the nature of the liquid take place which can best be explained by the breaking down of the nicotine hydrates.   Likewise, the values of K_c for the different solutions show no regularity of behavior.   No higher values are obtained in case of Solution No. 6 with a high nicotine content than with Solution 1, which has the lowest.

It is obviously futile to draw any conclusions as to the state of nicotine and water in the various solutions from a consideration of this change in molecular surface energy with temperature.   A much more fertile field of speculation is presented when the surface tensions are plotted against concentrations, as shown in Fig. 2.   There we have a series of maxima at about 36.15 and 72.16% which tend to disappear as the temperature rises.   Skalweit,[5] as mentioned before, observed a maximum density at a concentration of 72% of nicotine, Tsakalotos[4] a viscosity maximum at 78%, and Jephcott[3] from the specific rotation of nicotine solutions found maxima at roughly 40 and 80% nicotine concentration.   Now according to Denison,[10] whenever extensive deviations occur from the straight-line law for mixtures, it is reasonable to assume the existence of a compound at the point of maximum deviation.   Also, according to Denison, such deviations as are shown in the figure can scarcely be due to the change in association of either solvent.   The most likely explanation of the maxima must then be that they represent the points of maximum concentration of nicotine hydrates which break down as the temperature approaches 60°.

[8] Walden and Swinne, Z. physik. Chem., 82, 290 (1913).

[9] Hildebrand, "Solubility," The Chemical Catalog Co., Inc., New York, p. 111.

[10] Denison, Trans. Faraday Soc., 8, 20–35 (1911).

Summary

1. The densities and surface tensions of nicotine have been measured from −50 to 94° and of nicotine–water solutions from −50 to 60°.

2. The Eötvös constant for nicotine is shown to be between 2.4 and 2.8 and nicotine does not appear to be associated.

3. Evidence for the existence of nicotine hydrates is shown by the concentration–surface tension curves.

VANCOUVER, B. C., CANADA

THE DISSOCIATION PRESSURE OF Fe4N

BY P. H. EMMETT, S. B. HENDRICKS AND STEPHEN BRUNAUER
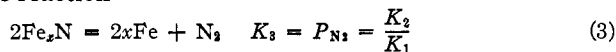
Introduction

In order to learn more concerning the various factors that contribute to the remarkable efficiency of promoted iron catalysts for the production of synthetic ammonia, a number of workers have investigated the conditions under which nitrides of iron can be formed. Baur and Voerman,[1] Maxted[2] and others tried without success to form iron nitride by the action of nitrogen at pressures as high as 200 atmospheres on iron between temperatures of 400 and 700°. Noyes and Smith[3] showed the possibility of calculating the exact dissociation pressure of the iron nitrides by combining the equilibrium constants for the reactions

$$N_2 + 3H_2 = 2NH_3 \qquad K_1 = \frac{(P_{NH_3})^2}{(P_{H_2})^3(P_{N_2})} \qquad (1)$$

$$2Fe_xN + 3H_2 = 2xFe + 2NH_3 \qquad K_2 = \frac{(P_{NH_3})^2}{(P_{H_2})^3} \qquad (2)$$
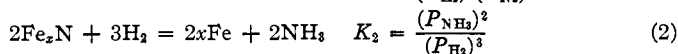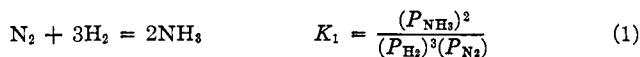
to obtain K_3 for the reaction

$$2Fe_xN = 2xFe + N_2 \qquad K_3 = P_{N_2} = \frac{K_2}{K_1} \qquad (3)$$

At 460° the indirect values thus obtained were found to vary between 20,000 and 500,000 atmospheres, depending upon the nature of the solid phase.

The surface hardening of complex alloy steels by treatment with ammonia at elevated temperatures enhances interest in equilibria for the iron–nitrogen system. Recent x-ray structure investigations by Hägg,[4] by Brill[5] and by Osawa and Iwaizumi[6] of the compounds formed by the action

[1] Baur and Voerman, *Z. physik. Chem.*, **52**, 467 (1905).

[2] Maxted, *J. Soc. Chem. Ind.*, **37**, 105 (1918).

[3] Noyes and Smith, THIS JOURNAL, **43**, 475 (1921).

[4] Hägg, *Nature*, **121**, 826 (1928).

[5] Brill, *Z. Kryst.*, **68**, 378 (1928).

[6] Osawa and Iwaizumi, *ibid.*, **69**, 26 (1928).