TABLE II

Molal	$K = 2 \times 10^{-2}$			$K = 1 \times 10^{-2}$			$K = 7 \times 10^{-3}$		
	α	β	$-E_0$	α	β	$-E_0$	α	β	$-E_0$
0.005016	0.728	0.872	0.1255	0.569	0.877	0.1296	0.473	0.880	0.1324
.01003	.653	.846	.1249	.486	.854	.1299	.395	.858	.1330
.02007	.564	.812	.1241	.396	.819	.1300	.313	.828	.1335
.05023	.442	.757	.1246	.286	.771	.1314	.217	.778	.1353
.1006	.359	.708	.1264	.219	.723	.1336	.163	.730	.1377

TABLE III

Molarity	Density 25/4	Molality	$E_{obs.}$	$-E_0'$	$\gamma_{H_2SO_4}{}^a$	$\gamma_{H_2SeO_4}$
0.00500	0.99761	0.005016	+0.07413	0.10814	0.637	0.574
.01000	.99823	.01003	.05540	.10218	.543	.492
.02000	.99933	.02007	.03690	.09496	.452	.408
.05000	1.0027	.05023	.01250	.08459	.338	.312
.1000	1.0083	.1006	− .00643	.07694	.263	.255

[a] Interpolated from data of Harned and Hamer, THIS JOURNAL, **57**, 27 (1935).

Molal Electrode Potential.—The molal electrode potential has been calculated from the extrapolated value −0.1295 volt, the potential referred to the quinhydrone electrode. The standard potential for the cell

(Pt) H_2 | H_2SeO_4, Ag_2SeO_4 | Ag
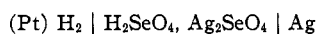
is −0.8289 volt, assuming E_0 for quinhydrone −0.6994 volt. This yields for the standard potential of the Ag–Ag_2SeO_4 electrode at 25°

Ag | $Ag_2SeO_4(s)$, $SeO_4^=$, E_0 = −0.8289 volt
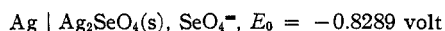
Summary

1. Electromotive forces of cells, QH | H_2SeO_4, Ag_2SeO_4 | Ag, have been measured at 25° in concentrations of selenic acid ranging from 0.005 to 0.1 molar.

2. A new method for determining E_0 has been presented.

3. The secondary ionization constant for selenic acid has been approximated: 1×10^{-2}.

4. The standard electrode potential, Ag | Ag_2SeO_4, $SeO_4^=$, has been determined: E_0 = −0.8289 volt.

5. The solubility of silver selenate in water and in selenic acid solutions has been determined.

Freezing Points of Binary Mixtures of Diphenylamine and Other Organic Compounds

BY O. A. NELSON AND L. E. SMITH

In the search for a material that would prevent wounds of livestock from becoming infested with larvae of the screwworm (*Cochlyomia americana* C. and P.), Bushland[1] tested a number of organic compounds. Among the compounds that appeared promising when applied in the form of a dry powder or dust in small-scale field tests were diphenylamine, phenoxathiin (phenothioxin), *p*-nitrophenetole, 1-nitronaphthalene, dibenzofuran, and phenothiazine. With the exception of phenothiazine all of these compounds have a low melting point, and mixtures of them were found to liquefy or become pasty at room temperature.

While some of the compounds are more effective at lower concentrations, diphenylamine possesses a number of desirable properties from a practical point of view, such as availability and cost. It was deemed desirable, therefore, to determine the freezing points of binary mixtures of diphenylamine with the other compounds.

Experimental

The compounds were purified as follows.

Diphenylamine.—Distilled under vacuum and then recrystallized three times from ligroin, b. p. 70–90°; m. p. 52.8–53.0°.

Phenoxathiin (commercial).—Distilled under reduced pressure and then recrystallized from ethyl alcohol; m. p. 55.3–55.5°.

***p*-Nitrophenetole** (purified).—Recrystallized twice from petroleum ether; b. p. 40–60°; m. p. 57.8–58°.

1-Nitronaphthalene (purified).—Recrystallized twice from ligroin; b. p. 70–90°; m. p. 55.8–56.0°.

(1) R. C. Bushland, *J. Econ. Ent.*, **33**, 666, 669 (1940).

TABLE I

FREEZING POINTS OF BINARY MIXTURES CONTAINING DIPHENYLAMINE

Concn. of diphenylamine, mole per cent.	Phenoxathiin		p-Nitrophenetole		l-Nitronaphthalene		Dibenzofuran		Phenothiazine	
	Crystn.	Obsd. eutectic	Crystn.	Obsd. eutectic	Crystn.	Obsd. eutectic	Crystn.	Obsd. eutectic	Crystn.	Obsd. eutectic
100.0	52.8		52.8		52.8		52.8		52.8	
97.0									51.1	49.4
90.0	48.4		48.3		48.4		48.3		66.4	49.3
80.0	43.6	26.4	43.7		43.6		43.1	34.5	95.1	
70.0	38.4	26.4	37.1		37.4		39.4	34.5		
60.0	32.6	26.4	29.4	24.5	31.1	23.8	39.4	34.6		
55.5	30.8	26.4	24.3	24.3						
50.0	26.7	26.4	28.4	24.3	23.8	23.7	49.5	34.6	144.4	
40.0	34.1	26.4	36.9		32.4	23.7	57.3			
30.0	40.5		43.7	24.3	40.1		65.1			
20.0	45.9		49.3		46.6		71.7			
10.0			54.1		51.3		77.0		178.4	
0.0	55.4		57.9		55.8		81.9		185.1	

Dibenzofuran (commercial).—Distilled in a high vacuum, and then recrystallized twice from alcohol; m. p. 81.8–81.9°.

Phenothiazine (commercial).—Recrystallized twice from toluene, using Norit, followed by sublimation at approximately 1 mm. pressure; m. p. 185.0–185.3°.

The temperature at which crystals began to separate from the mixture and the eutectic temperature of the system were determined by the method used in the determination of the freezing point of phenothiazine.[2]
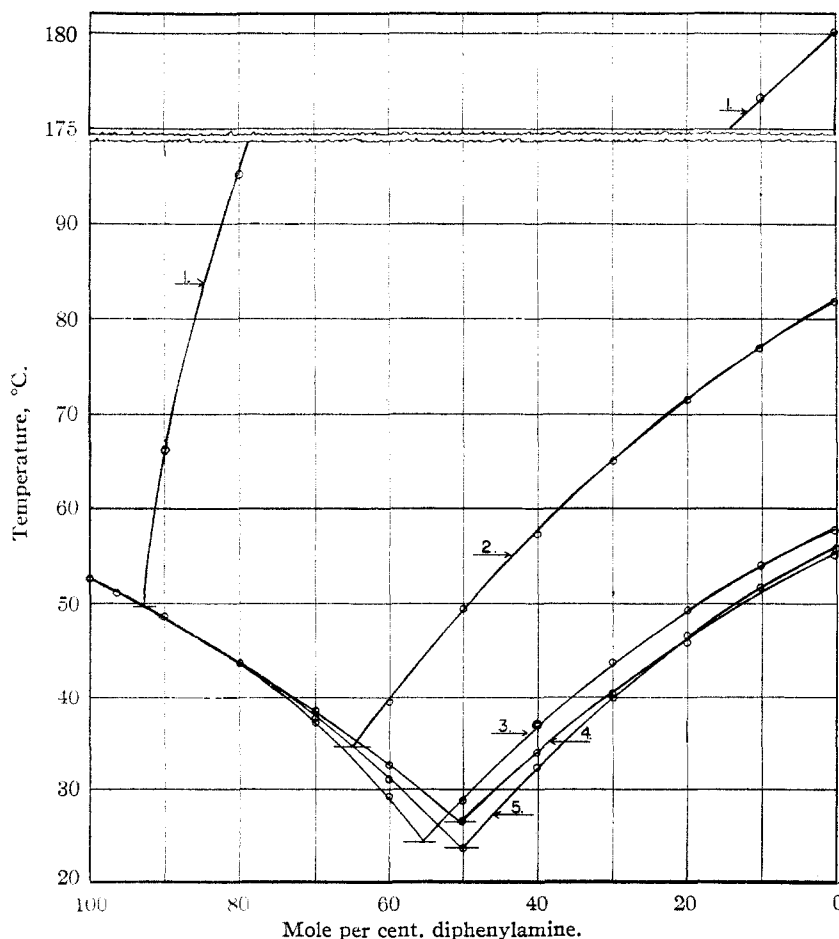
Results

The results obtained in these determinations are tabulated in Table I and shown graphically in Fig. 1. Attention is directed to the eutectic temperatures, three of which were found to be in the range of ordinary room temperature (23.7–26.4°), while the other two were somewhat higher (34.6–49.3°). This explains the observed liquefaction of some of the mixtures at room temperature.

Discussion of Results

The depression of the freezing point in binary systems is given by the equation

$$\log_e X = \left(\frac{Q}{R}\frac{1}{T_0} - \frac{1}{T}\right)$$

in which X is the mole fraction of solvent, Q is the molar heat of fusion, R is the gas constant in calories per mole, T is the crystallization temperature, and T_0 is the freezing point of the pure solid

Fig. 1.—Curves: 1, diphenylamine–phenothiazine; 2, diphenylamine–dibenzofuran; 3, diphenylamine–p-nitrophenetole; 4, diphenylamine–phenoxathiin; 5, diphenylamine–l-nitronaphthalene.

(2) L. E. Smith and O. A. Nelson, THIS JOURNAL, 64, 461 (1942).

phase (both temperatures in absolute degrees).

This equation is valid over the entire range of temperature and composition from the freezing point of the pure component to the eutectic temperature, if the solution is ideal and Q is constant. According to this equation the plot of log X against $1/T$ will be a straight line. When the data recorded in Table I were plotted in this manner, it was found that only in the system diphenylamine–phenoxathiin did straight lines result when both components were considered as solvents. In the system diphenylamine–dibenzofuran, a straight line resulted when dibenzofuran was taken as solvent. In all other cases the curves deviated in varying degrees from a straight line particularly at the higher concentration of solute, that is, near the eutectic concentrations.

From the data obtained in these experiments the freezing point constants—that is, the freezing point lowering, in degrees centigrade, per mole of solute dissolved in 1000 g. of the solvent—were calculated for the six compounds worked with. The values obtained were: diphenylamine 6.55, phenoxathiin 7.7, p-nitrophenetole 5.7, 1-nitro-

naphthalene 6.5, dibenzofuran 7.3 and phenothiazine 12.0. The eutectic temperatures and compositions are presented in Table II.

TABLE II
EUTECTIC COMPOSITIONS AND TEMPERATURES FOR BINARY SYSTEMS CONTAINING DIPHENYLAMINE

Other compound	Mole, %	Eutectic temp., °C.
Phenoxathiin	49.5	26.4
p-Nitrophenetole	44.6	24.3
1-Nitronaphthalene	49.8	23.7
Dibenzofuran	35.2	34.6
Phenothiazine	7.5	49.3

Summary

The crystallization temperatures, eutectic composition, and eutectic temperatures have been determined for the binary systems diphenylamine and phenoxathiin, diphenylamine and p-nitrophenetole, diphenylamine and 1-nitronaphthalene, diphenylamine and dibenzofuran, and diphenylamine and phenothiazine. From the data obtained the freezing point constants were calculated for the six compounds investigated.

WASHINGTON, D. C.   RECEIVED JANUARY 10, 1942

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Ketene Acetals. IX. Ketene Dialkylacetals

BY S. M. MCELVAIN AND P. M. WALTERS

The preparation of ketene diethylacetal by two distinctly different procedures[1] and the properties which this compound was found to possess have shown, beyond all doubt, that the claims of Scheibler and associates[2] to have isolated this substance from the reaction of sodium and/or sodium ethoxide with ethyl acetate are spurious. In spite of this fact it seemed worth while to prepare and record the correct properties of certain homologs of ketene diethylacetal which have been reported[3] from Scheibler's laboratory. One of these homologs, methylketene diethylacetal, $CH_3CH\!=\!C(OC_2H_5)_2$, has been described in the paper that dealt with the preparation of ketene acetals by the action of sodium on α-bromoorthoesters.[1c]

(1) (a) Beyerstedt and McElvain, THIS JOURNAL, **58**, 529 (1936); (b) Johnson, Barnes and McElvain, ibid., **62**, 968 (1940); (c) Walters and McElvain, ibid., **62**, 1482 (1940).

(2) Scheibler et al., Ber., **55**, 801 (1922); Ann., **458**, 15 (1927); THIS JOURNAL, **55**, 425 (1933).

(3) Scheibler, Marhenkel and Nikolic, Ann., **458**, 21 (1927).

The present paper reports the preparation and properties of ketene di-n-propyl-, di-isobutyl- and di-isoamylacetal. Each of these compounds was prepared by the elimination of hydrogen bromide from the corresponding dialkylbromoacetal by means of potassium t-butoxide according to the procedure reported in an earlier paper,[1b] thus

$$BrCH_2CH(OR)_2 + KOC_4H_9(t) \longrightarrow$$
$$CH_2\!=\!C(OR)_2 + KBr + t\text{-}C_4H_9OH$$
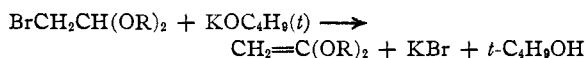
The boiling points of these homologous ketene acetals and of the corresponding esters of which the ketene acetals are the enol ethers are summarized in Table I. The boiling points of the ketene acetals as reported[3] by Scheibler and his collaborators are also included in this table. For comparison the corresponding values for ketene diethylacetal and methylketene diethylacetal which were reported earlier[1c] are given. It may be seen from these data that there is not only the marked