[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

Vapor Pressure of Binary Systems. I. Benzene and Acetic Acid

BY FRANK HOVORKA AND DALE DREISBACH

Introduction.—The benzene and acetic acid liquid system has been the subject of several investigations with conflicting results concerning the possibility of it belonging to a system having a maximum vapor pressure. Golodetz[1] described the separation of toluene from acetic acid by adding benzene, which formed an azeotropic mixture with the acetic acid. Lécat[2] reported a minimum boiling point of 80.05° for 97.5 mole per cent. benzene. Schmidt[3] applied the static method in a study of this system and reported a definite maximum vapor pressure at about 80 mole per cent. of benzene. On the other hand, the results recorded by the following investigators seem to indicate that this system belongs to a normal class of binary liquid mixtures having the usual deviations expected when structurally different substances are used. Linebarger[4] used the air saturation method and Rosanoff and Easley[5] a vapor bubbling method. Zawidski[6] and also Othmer[7] used the ordinary distillation method.

A preliminary investigation of this system was conducted by one of us[8] using the static method. The results obtained, although not complete, did not indicate a maximum vapor pressure. However, when the air saturation method was employed for the determination of the partial pressures, concordant results were not obtained.

In order to avoid some of the experimental difficulties inherent in existing methods, a new method was devised which embodies both the static and the dynamic principles, and from which it is possible to obtain both the partial and the total pressures of binary liquid systems.

Materials.—The best grade of thiophene-free benzene from Eastman Kodak Company was dried with sodium, distilled, and fractionally crystallized several times. The portion thus obtained was fractionally distilled. The fraction retained boiled at 80.23° and came over within 0.002° as measured with a ten junction copper–constantan thermocouple. The acetic acid from the Eastman Kodak Company was refluxed with the required amount of acetic anhydride according to the directions of Orton and Bradfield.[9] This was then fractionally distilled. The final fraction retained melted at 16.63 ± 0.01°.

Experimental Method.—The apparatus, Fig. 1, consists of a main tube B which serves as a receptacle for the original liquid mixture and is provided with a stirrer excited externally with an electromagnet G. C is a mercury manometer and side arm A has sealed onto it a set of sample bulbs. Each bulb can be filled with a portion of the original mixture by distillation, and sealed off. This makes it possible to obtain a set of readings starting with any desired mixture of the liquids.

About 10 cc. of the mixture was transferred to the apparatus in an atmosphere from which carbon dioxide and moisture had been removed. The solution was solidified with liquid air, the system evacuated and mercury introduced at D. Then the mixture was repeatedly melted, solidified and the system evacuated. The mercury in the manometer was heated during the evacuation in order to remove any dissolved air. After the final evacuation the apparatus was sealed off at E and F. The whole apparatus was then immersed in a constant temperature bath maintained at 25 ± 0.01°. After attainment of equilibrium the pressure was determined with a cathetometer capable of accuracy of 0.02 mm. of mercury. All readings were corrected to 0°. The side arm A was then removed from the bath and a fraction (about one-sixth of the total mixture when 6 sample tubes were used) very slowly distilled into the cooled sample tube 6, care being taken to maintain essentially equilibrium conditions during the distillation. The mixture and the remaining parts of the apparatus were kept at 25°. Tube 6 was then sealed off and arm A replaced in the bath and a pressure reading made on the solution remaining in B. This process was repeated until all of the original mixture was distilled into the sample tubes. The success of each run was determined by pressure readings at the end, no run being retained unless a zero reading was obtained.

The individual fractions were analyzed by measuring their refractive indices and comparing with a refractive index–composition curve prepared by Bauer.[10]

Discussion of Results.—The total and partial vapor pressures of various mixtures of acetic acid and benzene are shown in Fig. 2, along with some points interpolated from Schmidt's[3] data. The solid circles indicate a peculiar trend at the beginning of each set of points. The first readings are high and succeeding points are lower until finally the more general trend is reached (marked

---

(1) Golodetz, *J. Russ. Phys.-Chem. Soc.*, **43**, 1041 (1911).

(2) Lécat, "International Critical Tables," Vol. III, p. 319.

(3) Schmidt, *Z. physik. Chem.*, **121**, 221 (1926).

(4) Linebarger, THIS JOURNAL, **17**, 615 (1895).

(5) Rosanoff and Easley, *ibid.*, **31**, 953 (1909).

(6) Zawidski, *Z. physik. Chem.*, **35**, 129 (1900).

(7) Othmer, *Ind. Eng. Chem.*, **20**, 743 (1928).

(8) The senior author wishes to express his thanks to Professor W. H. Rodebush at whose suggestion this first study was made in 1925 at the University of Illinois.

(9) Orton and Bradfield, *J. Chem. Soc.*, **129**, 983 (1927).

(10) Thesis by I. B. Bauer, Western Reserve University, 1932.

with circles). These last points are in agreement with those from other runs in which part of the original sample had been distilled from the apparatus during the melting and solidifying process.

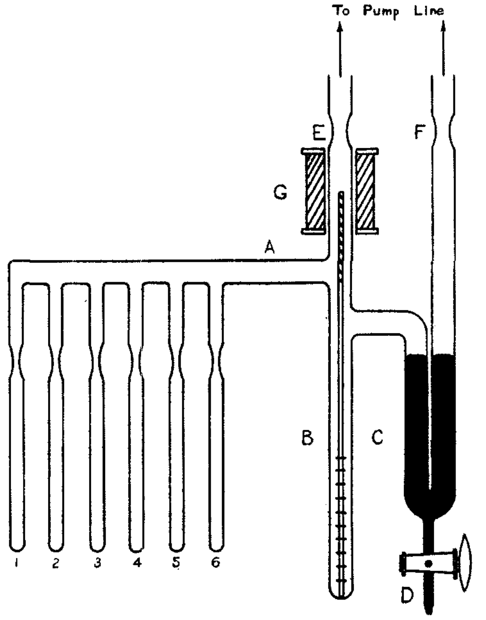

Fig. 1.—Apparatus.

In this way most of the dissolved gases are removed before any pressure readings were made. The points marked with squares were obtained using solutions of definite composition by weight, care being taken to prevent loss of any of the solution during evacuation. In these instances no distillation took place and hence no opportunity for the removal of absorbed gas in that manner. These pressures are quite high, and for mixtures rich in benzene they are higher than the vapor pressure of pure benzene. Moreover, the pressure does not come to a constant value with time but continues to drift toward higher values. That these phenomena are due mainly to dissolved air was demonstrated by using pure benzene instead of a mixture. Initially the pressure was high but decreased upon the removal of successive fractions, approaching a constant value, as shown by the following data.

Pressure of the original benzene sample	104.10 mm.
Pressure after fraction 1 was removed	96.53 mm.
Pressure after fraction 2 was removed	95.24 mm.
Pressure after fraction 3 was removed	95.00 mm.
Pressure after fraction 4 was removed	94.94 mm.

The refractive indices of these fractions were all identical with that of pure benzene. This effect, particularly with benzene, is in agreement with the fact observed by Lachowicz[11] that it is difficult to remove air which is dissolved in benzene. Also Smits and Swart[12] have shown the effect of dissolved gases on the vapor pressure, "it frequently being impossible to remove appreciable amounts of gas by repeatedly melting and solidifying the substance."

From these considerations the maximum obtained by Schmidt[3] may be partially explained by the fact that air was present in his system. Undoubtedly it is difficult to make an adequate correction for this air. Furthermore, it might be pointed out that his values for pure substances were not consistent. For example, in eight of the ten cases reported the vapor pressure of pure benzene at 30° was either 122.3 or 122 mm. and in the remaining two cases it was 113 and 116 mm. These last two values accentuate the maxima which he obtained for the acetic acid and benzene and the propyl alcohol and benzene mixtures.

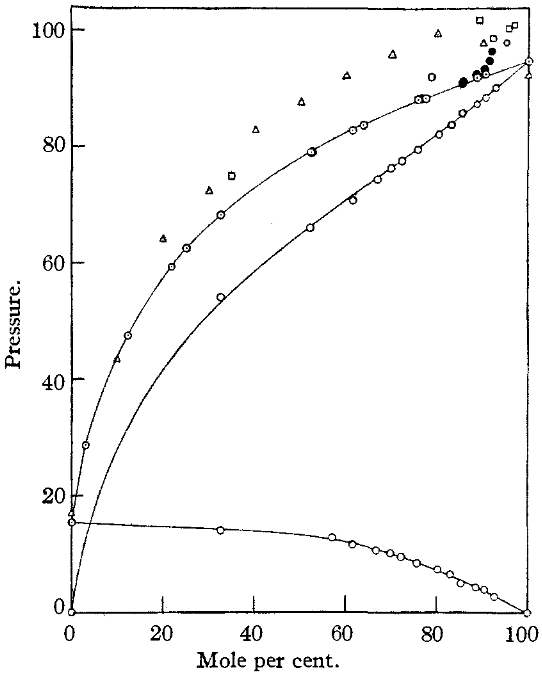

Fig. 2.—Plot of pressure against mole per cent. of benzene: ◉, observed; ●, effect of traces of dissolved air; ⊡, individual runs containing traces of air; △, Schmidt; ○, partial pressures.

The question of the miscibility of this system seems to have been satisfactorily decided by Linebarger,[13] any immiscibility being attributed

---

[11] Lachowicz, *Ber.*, **21**, 2206 (1888).

[12] Smits and Swart, *J. Chem. Soc.*, **31**, 2724 (1929).

[13] Linebarger, THIS JOURNAL, **17**, 932 (1895).

to impurities. No evidence of immiscibility was detected in this system but complete miscibility of some other systems, which have been reported as being azeotropic, has not been confirmed.

TABLE I

VAPOR PRESSURES OF ACETIC ACID AND BENZENE MIXTURES AT 25°

Mole per cent. benzene	Total pressure, mm.	Partial pressure acetic acid, mm.	Partial pressure benzene, mm.
0	15.43	15.43	0
3.1	28.63		
12.3	47.54		
21.8	59.46		
25.2	62.65		
32.6	68.38	14.2	54.2
52.1	79.17	13.0	66.2
52.6	79.19		
61.4	82.94	11.9	71.0
63.7	83.85		
66.8	85.56	10.9	74.7
69.8	86.88	10.4	76.5
72.2	87.5	9.7	77.8
75.6	88.37	8.7	79.7
77.4	88.45		
80.3	90.0	7.65	82.35
83.0	90.8	6.8	84.0
85.4	91.16	5.2	86.0
88.6	92.07	4.5	87.6
90.5	92.74	4.1	88.6
92.7	93.2	2.8	90.4
100.0	94.91	0	94.91

In the method here outlined the partial pressures (see Table I) of the two components were determined by the method of Rosanoff[14] and his collaborators, except that allowance was made for the weight of vapor in the apparatus.

As suggested by Othmer[7] this method results in the multiplication of quantitative errors. However, the greatest effect is on the first fractions since the calculations are made from the samples themselves and not the original mixture. These first readings are found also to be less reliable due to dissolved gases, and therefore should be given less weight than the last readings.

The fact pointed out in the introduction concerning the impossibility of obtaining concordant results in systems having benzene as one component, when using the air saturation method and condensing the vapor from the air with liquid air, may be emphasized in the light of some observations made recently in this Laboratory by Prof. R. E. Burk. It seems that small particles of solidified benzene will adsorb sufficient air to be carried through the liquid air trap and lost.

At present other binary systems are being studied, chiefly those that are classified as azeotropic.

Summary

1. A new method for the study of the total and partial vapor pressures of binary liquid mixtures is described. Total pressures can be readily obtained over a moderate temperature range. The difficulties due to dissolved gases and moisture are eliminated.

2. It has been confirmed that the acetic acid and benzene system is not azeotropic.

CLEVELAND, OHIO RECEIVED APRIL 26, 1934

---

[14] Rosanoff, Bacon and White, THIS JOURNAL, **36**, 1803 (1914).

[CONTRIBUTION FROM THE SPECTROGRAPHIC LABORATORIES, DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Studies on Chromium. III. The Occurrence of Chromium in Certain Soils and Plants in the Province of Quebec

BY ANDREW DINGWALL AND H. T. BEANS

The finding of chromium in human tumors[1] has led us to investigate the occurrence of chromium in solids and plants. Chromium has long been recognized as widely diffuse in the lithosphere, but we have only found three instances where it has been reported in plants in recent times.[2] The spectrographic technique we employed and the origin and treatment of the soil and plant specimens examined have been described elsewhere.[3]

Five soil specimens, surface and subsoil, ten specimens of vetch grown on different farms, two specimens of timothy, red clover, alfalfa and alsike, one specimen of goldenrod, reed canary grass, field corn stalks, ragweed and Canada thistle, and the ash from the liver of a rabbit fed on reed canary grass and distilled water were examined. Chromium was found in all cases.

---

[1] A. Dingwall and H. T. Beans, *Am. J. Cancer*, **16**, 1499 (1932).

[2] E. Demarcay, *Compt. rend.*, **130**, 91 (1900); W. O. Robinson, L. A. Steinkoenig and C. F. Miller, U. S. Dept. of Agriculture Bull., 600 (1917); L. Gouldin, *Chem. News*, **100**, 130 (1909).

[3] A. Dingwall, R. R. McKibbin and H. T. Beans, *Can. J. Research*, July (1934).