[CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

The Spreading of Binary Mixtures of Volatile Organic Liquids on Water

BY CHRIS P. KEIM[1] AND E. ROGER WASHBURN

It has been known that the spreading coefficient of an organic liquid may be changed if even a small amount of another substance is present. Hardy,[2] among others, showed that impurities in a non-spreading liquid may cause it to spread. Harkins and Feldman[3] reported the spreading effects resulting from the addition of a drop of oleic acid to a large lens of petrolatum on the surface of water. Langmuir and Schaefer[4] used mixtures of oils to give the pressures they desired when using indicator or piston oils. In general, however, quantitative results on the spreading coefficients of binary mixtures of organic liquids at various compositions have not been reported. In order to determine such spreading coefficients by the usual method one would need the values of surface tension at the mixture–air interface and at the mixture–water interface for the various compositions of the mixtures.

A report was made recently from this Laboratory on the measurement, by means of a surface film balance, of the spreading pressures of pure organic liquids put on unimolecular surface films on water.[5] Interesting results were obtained when this same technique was used in the study of the spreading pressures of binary mixtures.

Materials.—Stearic acid, benzene, nitrobenzene, toluene, and the redistilled water as previously described[5] were used. In addition, the following spreading materials were used: cyclohexane, Eastman Kodak Co. grade, m. p. 6.3°, b. p. 79.0° at 735 mm., d^{20}_4 0.7797, n^{20}_D 1.4244; bromobenzene, Eastman grade, d^{20}_4 1.5002, n^{20}_D 1.5576.

Apparatus.—The same film pressure apparatus as described before[5] was used in this work.

Procedure

A unimolecular film was put on the water by means of a solution of stearic acid in benzene. The film was slowly compressed by the movable barrier. At various pressures of the film a small drop of the binary mixture was put on the film. The liquid spread, often separating into two portions, pushed back the unimolecular film and increased the pressure reading of the balance. As drops of the mixture were added at increased film pressures the spreading decreased, the spreading liquid acquiring the form of a thin lens of small diameter and appearing to be of homogeneous composition. A film pressure could be reached where added drops did not spread and did not affect the balance reading. Thus, as with pure liquids, a film pressure was obtained which was considered to be the maximum spreading pressure of the mixture.

Rather early in this work on mixtures it became apparent that there were certain differences in the experimental procedure for the study of mixtures and of pure liquids. The spreading pressure of the added liquid mixture must be measured before any of either component has evaporated, thereby altering the composition of the mixture. If the liquid spreads to form a thin film, evaporation of either or both components may be rapid. The vapor pressure and the spreading tendency of each component are factors in this evaporation.

In an open dish the volatile spreading mixture often separates into two portions. For example, at certain unimolecular film pressures a mixture of benzene and nitrobenzene forms a thin film with droplets regularly spaced around the edge of the film. If a cover is placed over the dish this film–droplet arrangement immediately pulls into a homogeneous lens. This behavior can be controlled at will by removing or replacing the cover until one of the components has almost entirely evaporated from the surface. With a unimolecular film pressure great enough this separation will not appear and the added drop of the mixture remains in the lens form.

Because of the large cabinet enclosing the equipment, the procedure followed in measuring the spreading pressures of mixtures was practically equivalent to the "open dish" conditions.

Results

The spreading pressures of benzene–toluene, benzene–nitrobenzene, benzene–cyclohexane, ben-

---

[1] Samuel Avery Research Fellow, 1939–1940.

[2] Hardy, *Proc. Roy. Soc.* (London), **A88**, 313 (1913).

[3] Harkins and Feldman, THIS JOURNAL, **44**, 2665 (1922).

[4] Langmuir and Schaefer, *Chem. Rev.*, **24**, 181 (1939).

[5] Washburn and Keim, THIS JOURNAL, **62**, 1747 (1940).

zene–bromobenzene, and toluene–nitrobenzene were measured at various compositions as shown in Table I.

TABLE I

Mole % benzene	Wt. % benzene	Pressure dynes/cm.	Mole % benzene	Wt. % benzene	Pressure dynes/cm.
Benzene–Toluene (20–24°)					
0.0	0.0	8.4	54.4	50.3	9.2
10.7	9.2	8.8	70.6	67.1	9.3
18.9	16.5	8.9	85.7	83.5	9.3
37.3	33.6	9.0	100.0	100.0	9.4
Benzene–Nitrobenzene (22–25°)					
0.0	0.0	3.6	69.3	58.8	10.7
10.5	6.9	5.0	77.1	68.2	10.8
19.1	13.1	6.3	82.1	74.5	10.8
27.5	19.5	7.4	85.5	79.1	10.7
36.8	27.0	8.8	87.1	81.2	10.6
46.1	35.2	9.7	89.3	84.2	10.5
53.3	42.7	10.2	91.8	87.8	10.3
60.6	49.4	10.6	100.0	100.0	9.4
Benzene–Cyclohexane (21.5–23°)					
7.7	7.2	0.7	38.0	36.0	5.9
10.7	10.3	1.3	44.4	42.5	6.6
13.3	12.3	2.0	55.6	53.6	7.6
14.4	13.9	1.9	67.5	66.0	8.7
14.5	13.9	1.9	75.4	73.8	9.1
19.5	18.3	3.1	85.8	85.0	9.4
22.8	21.6	3.6	100.0	100.0	9.4
30.7	29.1	5.0			
Benzene–Bromobenzene (21–24°)					
30.6	17.9	2.1	54.1	36.9	5.1
32.2	19.1	2.5	60.6	43.2	5.4
33.8	20.2	2.8	61.4	44.0	5.7
36.9	22.6	3.0	70.0	53.8	6.7
43.4	27.8	3.5	70.2	53.9	6.7
44.4	28.4	3.8	76.4	62.0	7.5
47.2	30.8	4.1	80.5	68.3	7.6
47.8	31.4	4.1	85.2	74.3	8.2
53.6	33.6	4.7	100.0	100.0	9.3
Toluene–Nitrobenzene (21–25°)					
Toluene	Toluene		Toluene	Toluene	
0.0	0.0	3.7	78.5	73.3	10.6
7.2	6.2	5.4	79.3	73.9	10.6
8.3	6.3	5.5	79.8	74.4	10.6
15.9	12.3	6.7	79.8	74.7	10.5
21.4	16.7	7.7	83.1	78.3	10.4
32.3	26.5	9.1	85.0	80.9	10.3
38.4	32.5	9.5	85.2	81.3	10.3
49.5	42.3	9.9	90.5	87.4	10.0
65.3	58.8	10.2	95.0	93.3	9.8
70.7	64.4	10.4	98.5	97.7	9.3
74.6	68.6	10.6	100.0	100.0	8.5

It is interesting to observe the curves which are obtained when spreading pressures are plotted against composition of the mixtures. With the toluene–benzene mixture the measured spreading pressures are slightly above a straight line connecting the spreading pressures of the pure components. In the case of benzene–nitrobenzene the measured spreading pressures are much higher than if they followed a straight line relationship between the spreading pressures of the pure components. The maximum spreading pressure for this mixture is reached at about 78 mole per cent. benzene. Toluene–nitrobenzene mixtures give a curve similar to benzene–nitrobenzene and the maximum spreading pressure is between 75 and 80 mole per cent. toluene. The curve for cyclohexane–benzene shows no maximum and the spreading pressures at compositions increasing in cyclohexane show a trend toward a negative spreading pressure for pure cyclohexane. With bromobenzene–benzene the measured spreading pressures also show a trend toward a negative spreading pressure for pure bromobenzene.

These observations with bromobenzene and cyclohexane are interesting because bromobenzene and cyclohexane do not spread on a clean water surface. With increasing concentrations of bromobenzene or cyclohexane with benzene the spreading pressure decreases until a concentration is reached where the added drop stays as a lens no matter how small the unimolecular film pressure. The balance shows no change in pressure as the drop is added, but the lens moves about on the surface of the water. By compressing the film a pressure is obtained which just stops such a lens from moving or migrating. For a particular mixture "no spreading" pressure values and "no migrating" pressure values when plotted against composition give a continuous smooth curve. Inasmuch as the migrating of the drop is probably caused by local changes in surface tension about the periphery, indicating a tendency for spreading, the pressure at which migration just ceases may be the best measurement of spreading pressure. With benzene–bromobenzene and benzene–cyclohexane "no migrating" pressures were encountered at unimolecular film pressures below 3 dynes per centimeter.

Discussion

Since a straight line does not result from plotting our experimental spreading pressures against composition it is concluded, from the Harkins equation,[3] $S = \text{S. T.}_A - (\text{S. T.}_B + \text{S. T.}_{AB})$, that the curves relating surface tension to composition cannot be straight lines. This deduction coincides with literature data on such binary mixtures as benzene–nitrobenzene and toluene–nitrobenzene.[6,7]

In the above equation, S is spreading coefficient in dynes per centimeter, $S. T._A$ surface tension at the water–air interface, $S. T._B$ surface tension at the organic mixture–air interface, and $S. T._{AB}$ surface tension at the organic mixture–water interface. Using our measured values for S and data due to other experimenters for $S. T._A$ and $S. T._B$, good agreement is obtained between our values of $S. T._{AB}$ and those due to Bartell and Mack.[6]

In all the mixtures studied this general condition exists. If, when the mixture–air and mixture–water surface tension values are plotted against composition, the curves intersect, the composition–spreading pressure curve reaches a maximum, but if the surface tension–composition curves do not intersect the composition–spreading pressure curve does not reach a maximum. Also, when the spreading pressure–composition curves show a maximum, the composition at this maximum is practically the same as the composition where the respective surface tension curves intersect. Surface tension data for mixtures are limited and further conclusions will require information on surface tensions and spreading pressures for mixtures at various compositions.

Attempts were made to correlate the spreading pressures of mixtures with other physical properties, such as viscosity and vapor pressure. It might be expected that the curves resulting from plotting spreading pressure, viscosity, or vapor pressure against composition might be similar. However, no similarities were found. One reason for this might be in the fact that, in addition to the binary mixture, a third component, water, is always introduced in spreading pressure measurements by means of the surface film balance and a surface film on water.

Summary

1. Spreading pressures at various compositions of toluene–benzene, nitrobenzene–benzene, bromobenzene–benzene, cyclohexane–benzene, and toluene–nitrobenzene were measured by means of a stearic acid film and a film pressure balance.

2. For the mixtures studied the spreading pressure–composition curves show that the mixture–air surface tension–composition curve and the mixture–water surface tension–composition curve cannot be straight lines.

3. For benzene–nitrobenzene and toluene–nitrobenzene mixtures there is a close agreement between the composition at the intersection of the mixture–air surface tension–composition and the mixture–water surface tension–composition curves with the composition at the maximum spreading pressure on the spreading pressure–composition curve.

LINCOLN, NEBRASKA RECEIVED JUNE 17, 1940

---

[6] Bartell and Mack, *J. Phys. Chem.*, **36**, 65 (1932).

[7] "Int. Crit. Tables," Vol. IV, 1928, p. 473.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF DUKE UNIVERSITY]

The Electric Moments of Morpholine and Some Halogenated Toluenes[1]

BY ARTHUR A. MARYOTT, MARCUS E. HOBBS AND PAUL M. GROSS

In order to test further the validity of the vector bond moment addition method[1a] for determining the electric moment of molecules and to learn something of the possible influences of induction and resonance effects on the observed moment, six halogenated toluenes including 3,5-dichlorotoluene, 3,5-dibromotoluene, 2,4,6-trichlorotoluene, 2,4,6-tribromotoluene, 3,5-dibromobenzyl bromide, and *p*-chlorobenzotrichloride have been measured. The moment of morpholine also has been determined. For the data on *p*-chlorobenzotrichloride we are indebted to Dr. J. W. Jacokes.[2] All measurements were carried out as described previously[3] using essentially the same apparatus. A slight modification was made by changing the oscillating circuit to a grid-tuned type and by replacing each of the RCA 01 radio tubes with a type 37.

Materials

Benzene.—Kahlbaum best grade benzene was washed with concd. sulfuric acid, dried over phosphorus pent-

---

[1] Part of thesis of Arthur A. Maryott submitted in partial fulfilment of the requirements of the Ph.D. degree in Chemistry at Duke University, June, 1940.

[1a] Eucken and Meyer, *Physik. Z.*, **30**, 397 (1929).

[2] Jacokes, Ph.D. Thesis, Duke University (1936).

[3] De Bruyne, Davis and Gross, THIS JOURNAL, **55**, 3936 (1933).