

and ethylbenzene and for isopentane-*n*-pentane. The method is useful for systems to be used for determining the efficiency of distillation columns.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF MARYLAND]

Physical Properties of Some Organic Insect Repellents¹

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Under the Insecticide and Insect Control Research and Development Program carried out for the Department of National Defense, a large number of organic compounds were prepared and tested for their insect repellent effectiveness. It was thought that a critical study of the physical properties of some successful repellents might be of value in determining whether or not a correlation existed between repellent effectiveness and certain physical characteristics. However, the data required to make such a study were not available. We, therefore, were asked to provide certain physical data for a large number of compounds. The results which we have obtained up to the present are recorded in Table I.

Experimental

Purification of Materials.—About 25 to 30 ml. of starting material (all that was available) was vacuum distilled. A Vigreux column, 1 cm. diameter and 15 cm. long, provided with a chromel heating jacket, was used for all distillations except for isobutyric acid, α -hydroxy-, phenethyl ester and *dl*-malic acid, dibutyl ester. The middle fraction (50–60%) was collected under the conditions given in Table I.

Refractive Indices.—Measurements were made using an Abbe refractometer with temperature control. Check results agreeing to 0.0001 unit were obtained. The refractometer was calibrated against water (obs., 1.3325; lit., 1.3325) and with a test plate (obs. 1.5185; manufacturer's value for plate, 1.5185).

Boiling Points.—The boiling points were determined by a micro method.² The average of five to ten readings for each compound was always within 0.4° of the extreme readings. All boiling points were corrected to 760 mm. Based on the results for the reference materials listed in Table II and on the behavior of the test materials which did not decompose, we estimate the boiling points in Table I to be within 0.3°.

General Information for Remaining Measurements.—Due to the limited amounts of material available for the tests, it was necessary to design apparatus whose total volume was not over 2 cc. This necessitated the use of capillary tubing wherever possible. Such apparatus was usually cleaned with acetone, water, potassium chromate-sulfuric acid cleaning solution, water and distilled water. The apparatus was then dried with a current of clean dry air for about an hour while it was kept in the oven at about 45°.

Material was usually introduced into measuring apparatus by suction. All possible precautions to avoid picking up moisture in the course of an experiment were taken.

All thermostats (except the one used for refractive index measurements) were maintained at 35 ± 0.02°.

All thermometers were calibrated against thermometers previously calibrated by the Bureau of Standards.

After the test material was introduced into a measuring apparatus, the unit was allowed to come to temperature equilibrium in a minimum period of fifteen minutes.

Density.—Ostwald-Sprengel type pycnometers, volume about 1 ml., were used. Check weighings, agreeing to 0.1 mg., were made on a pycnometer and its contents. The precision is estimated to be 0.01%.

Viscosity.—Ostwald viscosimeters, volume between marks was 0.7 to 1.0 ml., were used. Five viscosimeters (small bore capillary) were calibrated with water, while one viscosimeter (large bore capillary) was calibrated with phthalimide, *N*-*s*-butyl-, after its viscosity was determined. The large bore viscosimeter was used for compounds whose viscosity was greater than 180 millipoises. The times of efflux on check runs agreed to 0.2%. Considering reproducibility and agreement with the value for benzene, we consider the results in Table I to be accurate to at least 0.2%.

Solubility.—The method discussed by Sobotka and Kahn³ was used. The test material is added drop by drop from a calibrated, water-jacketed, 1-ml. microburet, to a definite amount of water contained in a thermostated, glass-stoppered flask, until the end-point is reached (corresponding to the saturation of the water by the test material). Sudan IV was used as the indicator. From the density and volume of the material used, its solubility in grams per 100 ml. of water is calculated. The results, given in Table I, are based on duplicate runs.

A test run made on diethyl succinate gave a value of 1.73 g./100 ml. of water compared to a value of 1.78 g./100 ml. of water obtained by saponification with subsequent titration of a saturated solution of diethyl succinate in water. Benzyl alcohol, *p*-methoxy-, gave a solubility of 3.83 g./100 ml. of water compared to a value of 3.84 g./100 ml. of water obtained from a refractive index calibration curve.

Surface Tension.—In the first part of this work, measurements were made by the capillary tube method. The radius of each of six different tubes was determined using both benzene and water as standards. The results for each tube agreed to 0.5%. Heights of liquid in the tube and in the reservoir were measured with a cathetometer reading to 0.1 mm. A duplicate run was made on each material using a different capillary. The reproducibility of data and the agreement with the ring method used on phthalic acid, dimethyl ester and phthalimide, *N*-*s*-butyl-, indicate that the results given in Table I are within 1% in all cases and within 0.5% in the majority of cases (*i. e.*, those values not designated by the letter R).

Difficulty was experienced in getting equilibrium heights by the capillary tube method in the case of some of the compounds. In those cases, the surface tensions were measured by the ring method, using a Cenco du Noty precision direct tensiometer. The test liquid was placed in a weighing bottle surrounded by a jacket through which the bath water was circulated. The average of eight readings was used in each case to get the approxi-

(1) This research was carried out with funds provided by the U. S. Quartermaster Corps.

(2) Shriner and Fuson, "Identification of Organic Compounds," 2nd edition, John Wiley and Sons, New York, N. Y., p. 93.

(3) Sobotka and Kahn, *THIS JOURNAL*, **53**, 2935 (1931).

TABLE I
SUMMARY OF DATA

Compound ^d	Dist. range ^b in °C.	n_{25}^{20}	Density in g./ml.	Vis. in poise $\times 10^3$	At 35°		Surf. tens. in dynes/cm.	Interfacial tension against H ₂ O in dynes per cm.	B. p. in °C. at 1 atm. ^c
					Solubility in g./100 ml. of H ₂ O				
Acetoacetic acid, cyclohexyl ester	94-95	1.4615	1.0222	48.4	0.023 ± 0.004	32.9	13.1 ± 0.1	...	
Anthranilic acid, methyl ester	96-97	1.5810	1.1546	60.2	.290 ± .008	41.3	13.5 ± .1	...	
Benzaldehyde, <i>o</i> -ethoxy-	88-89.5	1.5409	1.0682	25.56	.116 ± .004	37.4	17.9 ± .05	...	
Benzoic acid, cyclohexyl ester	119.5	1.5200	1.0429	78.2	.001 ± .0006	35.7	26.8 ± .1	...	
Benzoic acid, tetrahydrofurfuryl ester	132-133	1.5209	1.1155	82.4	.098 ± .001	39.8	12.2 ± .1	...	
Benzyl alcohol, <i>o</i> -methoxy-	97-97.5	1.5460	1.1113	113.4	2.64 ± .03	42.3	5.54 ± .03	247.4	
Benzyl alcohol, <i>p</i> -methoxy-	102-103	1.5420	1.1017	93.2	3.83 ± .04	43.21R	4.08 ± .05	259.1	
Benzyl ether	125.5-126.5	1.5601	1.0341	37.11	0.0040 ± .0003	38.2	26.0 ± .2	...	
Bicyclo(2,2,1)-5-heptene-2,3-dicarboxylic acid, diethyl ester	117.5-118.5	1.4750	1.1074	100.6	0.354 ± .009	32.9	11.2 ± .1	...	
<i>cis</i> -Bicyclo(2,2,1)-5-heptene-2,3-dicarboxylic acid, dimethyl ester	114-115	1.4829	1.1637	150.2	1.32 ± .02	36.9	8.48 ± .04	...	
Cinnamic acid, isopropyl ester	107.5-108	1.5420	1.0046	57.9	0.004 ± .0005	32.7	
Cyclohexaneacetic acid, α -cyano-, ethyl ester	115-115.5	1.4590	1.0071	90.6	.033 ± .001	33.2	20 ± 2	...	
Cyclohexanecarboxylic acid, 1-hydroxy-cyclopentyl ester	107	1.4748	1.0486	147.0	.090 ± .002	33.8	12.8 ± 0.05	...	
Cyclohexanol, 2-phenyl-	107-108	1.5242	1.0053	340.7	.016 ± .001	35.7	16 ± 2	278.5	
4-Cyclohexene, 1,2-dicarboximide, <i>N</i> -butyl-	123.5-124	1.5001	1.0723	299.6	.226 ± .0006	34.7	11.4 ± 0.1	...	
<i>m</i> -Dioxane, 4-(<i>p</i> -methoxyphenyl)-5-methyl-	134	1.5266	1.1053	317.6	.144 ± .003	39.2	15.2 ± .1	...	
<i>m</i> -Dioxane, 5-methyl-5-nitro-2-propyl-, ^a	110.5-111	1.4518	1.1103	143.1	.300 ± .002	34.3	18.8 ± .2	...	
1,4-Dioxaspirodecane-3-methanol, 6-methyl-	103-104	1.4713	1.0678	450	.422 ± .001	32.8	3.05 ± .03	...	
1,3-Dioxolane, 2-hexyl-4-hydroxymethyl-	106-111	1.4490	0.9768	131.4	.157 ± .005	28.56R	2.98 ± .02	...	
1,3-Dioxolane, 2-hexyl-4-methoxymethyl-	89-90.5	1.4465	1.0027	31.43	.006 ± .0004	28.6	249.5	
Ethanol, 2-phenoxy-, acetate	97.5-98.5	1.5083	1.0908	53.0	.188 ± .004	37.8	11.1 ± .1	257.2	
Ethanol, 2,2'-thiodi-, diacetate	118-118.5	1.4675	1.1270	52.0	2.156 ± .003	36.5	7.66 ± .05	...	
Glycidic acid, β -methyl- β -phenyl-	112-113	1.5344	1.1141	159.1	0.119 ± .002	38.1	7.3 ± .1	...	
1,3-Hexandiol, 2-ethyl-	100	1.4490	0.9300	678	1.027 ± .002	29.02R	4.6 ± .05	243.4	
Hydraerylic acid, β -phenyl-, ethyl ester	123.5-124	1.5075	1.0881	148.2	0.805 ± .005	35.8	8.4 ± .1	...	
Isobutyric acid, α -hydroxy-, phenethyl ester	110-116	1.4950	1.0486	91.0	.501 ± .006	34.5	6.17 ± .05	268.6	
<i>dl</i> -Malic acid, dibutyl ester	111-120	1.4386	1.0228	85.4	.057 ± .002	29.2	9.5 ± .05	...	
2-Naphthol, 1,2,3,4-tetrahydro-	110	1.5625	1.0784	927	.519 ± .003	41.97R	8.0 ± .1	268.6	
1,5-Pentanediol dipropionate	106.5-107.5	1.4286	0.9815	28.12	.127 ± .002	30.6	14.4 ± .1	269.6	
Phenethyl alcohol, <i>p</i> -isopropyl-	100.5-101	1.5169	0.9599	150.9	.0896 ± .0003	32.49R	10.4 ± .1	258.2	
Phthalic acid, dimethyl ester	116-116.5	1.5137	1.1789	89.0	.430 ± .005	40.2	11.7 ± .05	283.6	
Phthalimide, <i>N</i> - <i>o</i> -butyl-	120-121	1.5417	1.1045	177.8	.025 ± .001	36.63R	19.0 ± .1	294.9	
1,2-Propanediol, 3-(1,3-dimethylbutoxy)-	104.5-106	1.4419	0.9544	309.7	.991 ± .002	25.7	
Propanol, 2-(2-cyclohexoxypropoxy)-	105.5-106.5	1.4530	0.9603	101.0	1.02 ± .05	31.1	6.00 ± .05	...	
Succinamic acid, <i>N,N</i> -diethyl-, propyl ester	124.5-125.0	1.4509	0.9876	56.8	5.20 ± .13	31.7	2.40 ± .05	...	
Succinamic acid, <i>N,N</i> -dipropyl-, ethyl ester	130.5-131	1.4517	0.9765	71.7	1.843 ± .005	30.8	6.3 ± .15	...	
Succinimide, <i>N</i> -amyl-	110-111	1.4721	1.0283	131.5	1.33 ± .02	33.35R	

^a *m*-Dioxane, 5-methyl-5-nitro-2-propyl-, is a solid, m. p. 46.5-47.1°. On fractionation, it formed a supercooled liquid. All the data were obtained on the supercooled liquid. ^b The majority of the compounds were distilled at 2 mm. pressure. Compounds 10, 26, 27, 32 in the order listed were distilled at 3.8 mm., 1-2 mm., 0.1-0.3 mm. and 2.4 mm. respectively. ^c Compounds, whose boiling points are not given, decomposed on heating. ^d Source of compounds, numbering them in the order listed in the above table: #26 from American Cyanamid; #12 from Columbia University; #4, 8, 14, 21 from Dow Chemical; #15 from du Pont; #2, 3, 7, 30, 31 from Eastman; #18 from Givaudan-Delawanna; #6, 16, 22, 28 from Harvard U.; #17, 23 from Ohio U.; #9, 10 from Sowa Chemical; #24, 33, 34 from Union Carbide & Carbon; #11, 32 from U. S. Department of Agriculture; #1, 13, 19, 20, 25, 27, 29, 35, 36, 37 from U. of Maryland; #5 from U. of New Hampshire.

mate surface tension. This approximate value was then corrected by the method given by Harkins.⁴

The surface tensions, marked R in Table I, are the values obtained by the ring method. Based on reproducibility of data and on the agreement with the literature values for the reference materials given in Table II, the

surface tensions by the ring method are estimated to be accurate within 0.4%.

Interfacial Tension.—The interfacial tensions of the test material against water were measured by the drop-volume method.⁵ The volume of the pipet in terms of distance between divisions was determined by calibration with mercury. The position of the meniscus was determined with a cathetometer, reading to 0.1 mm. The

(4) (a) Harkins and Jordan, *THIS JOURNAL*, **52**, 1751 (1930).

(b) Weissberger, "Physical Methods of Organic Chemistry," Vol. I, Chapter VI, Interscience Publishers, New York, N. Y., 1945.

(5) Harkins and Humphrey, *THIS JOURNAL*, **38**, 228, 236 (1916)

TABLE II
PHYSICAL PROPERTIES OF REFERENCE LIQUIDS^a

Property	Compound	Exp.	Lit.
Viscosity	Benzene	5.27, 5.26	5.26 ^b
Surface tension (R)	Water	70.56	70.85 ^{4b}
	Benzene	26.83	26.89 ^e
B. p.	Nitrobenzene	210.9	210.9 ^d
B. p.	Decalin	193.3	193.3 ^d
B. p.	Ethylene glycol	197.4	197.5 ^d
B. p.	<i>p</i> -Methoxy benzyl alcohol	259.1	258.8 ^d
Interfacial tension at 20°	Chloroform	29.7 ± 0.5	32.8 ^e
	Chlorobenzene	35.5 ± 0.2	37.4 ^e
Interfacial tension at 35°	Carbon tetrachloride	43.2 ± 0.5	43.5 ^e

^a Units and experimental conditions are the same as in Table I unless otherwise specified. ^b "I. C. T.," Vol. V.

^c Hennaut-Roland and Lek, *Bull. soc. chim. Belg.*, **40**, 177 (1931); *C. A.* **25**, 5323 (1931). ^d "I. C. T.," Vol. I. ^e "I. C. T.," Vol. IV.

method of calculation of interfacial tension, including the use of a correction factor was that of Harkins.^{4b} Table II indicates the comparison between our values and the literature values for several liquids. The agreement is as close as that reported by investigators using different experimental procedures.⁶ The interfacial tension values for those liquids whose densities are only slightly different from that of water were either not determined, or if made, the precision was poor.

Summary

Physical constants for a large number of organic insect repellents were determined.

(6) Andreas, Hauser and Tucker, *J. Phys. Chem.*, **42**, 1001 (1938).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

The Use of Radioactive Tracers in a Study of Activator Distribution in Infrared-Sensitive Phosphors^{1,2}

BY R. W. MASON, C. F. HISKEY AND ROLAND WARD

The preparation and some of the properties of infrared-sensitive phosphors of the alkaline earth sulfides and selenides have been described by Urbach,³ Smith,⁴ Primak⁵ and Stripp.⁶ It has been found that reproducible samples are most conveniently prepared by the use of presumably non-reactive fluxes such as lithium fluoride or strontium chloride. The flux effects a complete recrystallization of the base material⁵ and serves to introduce the activators during the recrystallization. Since the luminescent properties are quite sensitive to variation in the concentration of the activators, the relationship between these and the brightness of the phosphors under stimulation was investigated.⁶ While the results were empirically satisfactory, the absolute activator concentration was not known since the activators at equilibrium conditions must be distributed between the base and the flux. The determination of distribution coefficients of rare earth ions at such low concentrations (0.02% or less) in alkaline earth compounds would be very difficult by the usual analytical procedures, but the avail-

ability of radioactive isotopes of europium, cerium and samarium offered a possible solution.

The main difficulty in the application of the tracer technique lay in the separation of the intimately mixed phases. A separation method based on the difference in specific gravities of the base and flux was only partially successful. A much more satisfactory procedure was devised which involved filtration at the fluxing temperature (about 1000°) using a platinum Munroe crucible. Since the method may find some application in studying solubility phenomena in molten salt systems, the procedure is described here in some detail.

Experimental

Materials.—Strontium sulfide and selenide were prepared as previously reported.^{3,4} The fluxes, strontium chloride and lithium fluoride, contained only spectroscopic traces of the other alkaline earths and the alkali ions.

Procedure

(1) **Separation of Base and Flux by Filtration.**—The preparation of a Munroe crucible has been described by Snelling⁷ and Swett.⁸ Although the platinum mat is reasonably resistant to attack by the phosphor mixtures at 900 to 1100° in a nitrogen atmosphere, it eventually develops pinholes or cracks. These may be sealed by dipping in chloroplatinic acid and heating at 500° or by decomposing a layer of ammonium chloroplatinate on the mat and burnishing and compressing with a glass rod.

The mixtures containing strontium chloride separated readily by gravity filtration but those containing lithium fluoride required suction. For this purpose the apparatus shown in Fig. 1 was constructed. A smooth flange was forged on the Munroe crucible (1) and one end of the

(1) The work described in this paper was carried out under Contract NObs 39045 between the Bureau of Ships and the Polytechnic Institute of Brooklyn.

(2) Abstracted from a thesis by R. W. Mason submitted to the Graduate School of the Polytechnic Institute of Brooklyn, 1948, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) F. Urbach, D. Pearlman and H. Hemminger, *J. Optical Soc. Am.*, **36**, 372 (1946).

(4) A. L. Smith, R. D. Rosenstein and R. Ward, *THIS JOURNAL*, **69**, 1725 (1947).

(5) W. Primak, R. K. Osterheld and R. Ward, *ibid.*, **69**, 1283 (1947).

(6) K. F. Stripp and R. Ward, *ibid.*, **70**, 401 (1948).

(7) W. O. Snelling, *ibid.*, **31**, 456 (1900).

(8) O. D. Swett, *ibid.*, **31**, 928 (1909).