intensity curve is very insensitive to bond angle which they estimate as 122 ± 5°.

Using various values of d within the limits of 1.46 ± 0.02 Å. we have calculated the corresponding bond angles. The results are given in Table X.

TABLE X

DETERMINATION OF THE BOND ANGLE OF THE SULFUR DIOXIDE MOLECULE

$d \times 10^8$ cm.	$2\theta°$
1.44	125.2 ± 0.4
1.45	127.1 ± .4
1.46	128.9 ± .4
1.47	130.6 ± .4
1.48	132.1 ± .4

On the basis of the data in Table X the most reliable value of the bond angle is taken as 129 ± 4°.

We thank Dr. Roy Overstreet for assistance with the experimental measurements.

Summary

The heat capacity of solid and liquid sulfur dioxide has been determined from 15°K. to the boiling point.

The melting and boiling points were found to be 197.64 and 263.08°K., respectively.

The heats of fusion and vaporization were measured calorimetrically and found to be 1769.1 and 5960 calories per mole, respectively.

The vapor pressure of sulfur dioxide was measured from the melting point to the boiling point. The observations have been represented by the equation: liquid SO_2, 197.64 to 263.5°K. (0°C. = 273.10°K.).

$$\log_{10}P(\text{inter. cm. Hg}) = -1867.52/T - 0.015865T + 0.000015574T^2 + 12.07540$$

From the calorimetric measurements, the entropy of sulfur dioxide gas at the boiling point, 263.08°K., was calculated to be 58.07 cal. deg.$^{-1}$ mole^{-1}. $S^{\circ}_{298.1} = 59.23$. This value, which is the most reliable value to use in thermodynamic calculations, agrees with the value calculated by Cross from available molecular data. The agreement is sufficient to show that the entropy of sulfur dioxide approaches zero at the absolute zero of temperature.

The experimental entropy value has been used to obtain a more reliable value of the bond angle of sulfur dioxide. The angle was calculated to be 129 ± 4°.

BERKELEY, CALIF. RECEIVED MARCH 21, 1938

[CONTRIBUTION FROM THE AMMONIA DEPARTMENT OF E. I. DU PONT DE NEMOURS & COMPANY, INC.]

Optical Crystallographic Studies with the Polarizing Microscope. I. Identification and Semiquantitative Determination of Acetic and Propionic *p*-Bromoanilides in their Binary Mixtures

BY W. M. D. BRYANT

The following investigation of optical properties and melting points in the binary system of acetic and propionic *p*-bromoanilides, serves as the basis of a method for the identification of small amounts of acetic and propionic acids either individually or in mixture, and in the latter case supplies a means of estimating in a semiquantitative way the relative composition. *p*-Bromoanilides are highly satisfactory as derivatives for the identification of fatty acids,[1,2] and in this capacity excel many of the more recently described acid derivatives from the standpoints of stability, ease of preparation and convenient spacing of the melting points. The present research dealing with two compounds of this group has offered a favorable opportunity for the microscopic investigation of a system of organic mixed crystals by the methods of optical crystallography and has provided an illustration of the highly specific type of information that may be gained by this kind of research.

The binary system under consideration involves a number of distinct crystalline solid phases. Acet-*p*-bromoanilide exists in at least three crystal modifications,[3] a stable and two metastable forms, while the propionic derivative is dimorphous. In addition to the pure components, metastable propion-*p*-bromoanilide forms a continuous series of mixed crystals with one of the three acetic polymorphs, extending down to

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(1) Robertson, *J. Chem. Soc.*, **115**, 1210 (1919).

(2) Kuehn and McElvain, THIS JOURNAL, **53**, 1173 (1931).

(3) (a) Gossner, *Z. Krist.*, **38**, 110 (1904); (b) Chattaway and Lambert, *J. Chem. Soc.*, **107**, 1766 (1915). Both references mention only two forms.

about 20% of the propionic derivative or less. Certain optical properties of this mixed crystal system, particularly optic axial angle, undergo large measurable changes of magnitude as the composition of the mixture changes. This is rendered more valuable by the presence of very strong dispersion, causing appreciable variation of the optic axial angle with wave length of monochromatic light and so introducing another criterion of composition.[4] Optical properties of the above polymorphs apparently have not been reported previously except in the case of the stable form of the acetic derivative for which some data exist.[5]

The present research is marked by certain departures from the usual practice of microscopic identification that favor the measurement of optical constants not generally regarded feasible with the microscope. An important departure is the use of oil immersion systems of high numerical aperture, permitting the measurement of the whole range of acute optic axial angles and even obtuse axial angles where these are not too large. Measurement of both optic axial angles of a crystal permits the direct calculation of the true angle, $2V$, by means of the relation, $\tan V = \sin H_a/\sin H_0$ without the use of the refractive index β. Use of highly convergent light also permits a correct determination of the optical character or optic sign where ordinarily considerable uncertainty might exist, and aids in the recognition of the principal refractive indices by means of interference figures. Many modern petrographic microscopes are suitably equipped for this work or may be rendered so by means of standard accessory equipment. This oil immersion technique is by no means restricted to observations on very small crystals, although its advantages in that connection are great. Where the facilities for observation and measurement of interference figures are good, the characterization and measurement of the various forms of crystal dispersion present little difficulty. These properties are particularly pronounced in organic compounds of the aromatic series. An important factor in the successful study of interference figures in this series is the use of strong monochromatic light, such as may be obtained from metal vapor lamps, in place of the mixed radiation of the usual incandescent lamp. The latter light source, however, is useful for qualitative examination and should not be abandoned.

Mixtures of the acet- and propion- derivatives differ from those of most other *p*-bromoanilides by apparently failing to form a eutectic. The melting points of the mixtures are almost as sharp as those of pure compounds and form a smooth curve without a minimum in the plot of melting point *versus* composition. The sensitive range of the curve is on the high acetic side, including those compositions not covered by the optical method. When the melting points in this binary system of polymorphic compounds are observed under the microscope, the phenomena are often quite complex, but by the usual macro methods only one melting point for each composition is ordinarily obtained.

Experimental

Preparation of the Derivatives.—Pure acet- and propion-*p*-bromoanilides were prepared from Eastman *p*-bromoaniline and the corresponding acyl chlorides by the method of Robertson[1] as modified by Kuehn and McElvain.[3] The derivatives were recrystallized from benzene, chloroform, absolute and 60% ethanol. Mixtures of the two derivatives were made in gram quantities, weighing to the nearest milligram. Each mixture was transferred to a small Pyrex test-tube, heated over a micro-burner until completely fused, and then quickly cooled by plunging the tube into a mixture of solid carbon dioxide and methanol. The rapid cooling produced mixed crystals involving the metastable propionic derivative and served to discourage tendencies of the mixtures to crystallize fractionally. The mixtures were scraped from the tubes and crushed to a coarse powder in an agate mortar, avoiding grinding in order to preserve the structure of the fragments. The same scheme was used in preparing the pure metastable propion-*p*-bromoanilide.

Apparatus and Technique.—A Bausch and Lomb LD petrographic microscope was used in the present research. Monochromatic light for the bulk of the observations was obtained from the mercury arc using the light filters recommended in previous articles[6] to isolate the required wave lengths of light. This light source was supplemented by a Bausch and Lomb monochromator, illuminated by means of a carbon arc, to supply narrow portions from the complete visible spectrum for use in the dispersion studies. White light for preliminary examination was supplied by a ribbon filament, incandescent lamp. The microscope, equipped with a Zeiss 7X linear micrometer ocular of the Huygens type, an oil immersion objective (1.9 mm., 1.25 N.A.) and an aplanatic condenser (N.A. 1.40), was calibrated for optic axial angle measurement with the aid of an Abbe apertometer.[7] This scheme of calibration is preferable

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[4] The writer [THIS JOURNAL, **55**, 3201 (1933)] previously has utilized the same optical constants in another mixed crystal system but covering a more restricted range of compositions.

[5] Groth, "Chemische Krystallographie," Vol. IV, Wilhelm Engelmann, Leipzig, 1917, p. 228, gives a few results chiefly by Mügge, *Z. Krist.*, **4**, 335 (1879).

[6] Bryant, THIS JOURNAL, **55**, 3201 (1933); *Am. Mineral*, **20**, 281 (1935).

[7] F. E. Wright, "The Methods of Petrographic Microscopic Research," Carnegie Institution Publication 158, Washington, 1911, p. 148.

TABLE I

OPTICAL CRYSTALLOGRAPHIC PROPERTIES OF ACET- AND PROPION-*p*-BROMOANILIDES

Derivative		$CH_3CONHC_6H_4Br$			$C_2H_5CONHC_6H_4Br$	
Polymorph		(I) Stable form	(II) Metastable	(III) Metastable	(I) Stable form	(II) Metastable
Crystal system		Monoclinic	Uncertain[a]	Uncertain	Orthorhombic	Uncertain
Optical orientation or elongation		Ax. pl. (010) (Groth)	Elong. ‖ β (Bx_a) ‖ γ (Bx_0)	Elong. ‖ β or γ (Bx_a) ‖ β (Bx_0)	Ax. pl. (001) Bx_a = a (Groth)	Uncertain
Refractive indices[b] at 25 ± 3° for λ = 5461 Å.	α	1.497	1.610		1.590	1.653
	β	1.663	1.678	1.68 ± 0.01	1.653	1.660
	γ	1.945	1.805		1.755	
Birefringence λ = 5461 Å.		0.448	0.195	Strong	0.165	Strong
Optical character		Positive	Positive	Negative	Positive	Positive
Optic axial angle λ = 5461 Å.	$2H_a$	97 ± 1°	80 ± 1°	97 ± 2°	87 ± 1°	78 ± 3°
	$2H_0$	108.5 ± 0.5°[c]	123 ± 5°	109 ± 4°	116 ± 3°	(See Table II)
	$2V$	85°[d]; 86°[c,e,f]	72°[d]; 71°[e]	85°[d,e]	78°[d,e]; 80°[f]	72°[e]
Dispersion		r > v, moderate	r > v, moderate	v > r, moderate	r > v, strong	v > r, very strong
Habit and method of preparation		Compact prisms and elongated plates from C_6H_6, $CHCl_3$ and abs. C_2H_5OH, after transformation of metastable (II) form. Occurs in crystalline films from fusion	First solid phase from warm C_6H_6, $CHCl_3$, CH_3COOH, abs. C_2H_5OH; best crystals from hot 60% C_2H_5OH in elongated plates and needles. Thin broad plates by sublimation. Also in films from fusion	Found only in crystallized melts along with I and II forms. Best obtained by rapid quenching	Elongated plates from hot 60% C_2H_5OH; also from hot C_6H_6, $CHCl_3$, and abs. C_2H_5OH	Obtained by rapid quenching of melt; habit compact

[a] Probably orthorhombic. [b] Precision ±0.003 except where noted. [c] Verified by stage goniometer. [d] Calculated by tangent formula using $2H_a$ and $2H_0$. [e] Calculated from $2H_a$ and β. [f] Calculated from α, β and γ.

to the usual one of employing standardized crystal preparations in conjunction with the Mallard relation, since it provides a complete, rapid, and precise empirical calibration of the optical system. As the magnitudes of the optic axial angles encountered in the present research were often too great to be expressed as $2E$ (the angle relative to air), the corresponding value relative to cedar oil, $2H$, was employed ($\sin H = \sin E/1.515$ = N.A./1.515). The magnitude of $2H$ measured with the above equipment is independent of the actual refractive index or dispersion of the cedar oil used for immersion contact, and depends only upon the value assumed for calibration purposes (n_D 1.515).[8] Optic axial angles were also measured by the familiar rotation method using a small stage goniometer[9] having the advantages of that described by Wood and Ayliffe,[10] but slightly more compact, hence better suited for use with the LD microscope.

Melting points were determined with the aid of a carefully calibrated Dennis melting point bar.[11] Temperatures were measured thermoelectrically using a special Leeds & Northrup portable potentiometer reading directly in degrees centigrade for copper–constantan thermocouples and graduated in units of 0.5°.

The optical investigation of the derivatives involved examination both as individual crystals or crystal fragments mounted in Canada balsam and as crystalline films prepared by melting some of the material on a microscope slide under a cover glass. In the case of the mixed crystal system the following scheme was found convenient. Small quantities of the crushed crystalline mixtures were each mounted in a drop of fairly thick natural Canada balsam on a 25 × 50 mm. micro slide and covered with a thin cover glass. At first using white light the suspended crystals were examined for the acute bisectrix interference figure of metastable propion-*p*-bromoanilide or its mixed crystals with the acetic derivative. Crystals of this modification showed abnormal polarization colors and, when properly oriented for observation, these colors were predominantly blue or blue green, with incomplete extinction. The corresponding interference figures were recognized by their very strong dispersion. When a suitable

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(8) The dispersion of cedar oil has been neglected. The maximum error introduced in this way does not exceed 1% of $2H$ or an absolute error of about 1° for large values of $2H$, hence is generally negligible even when monochromatic radiation from the violet is employed.

(9) This instrument was made to the writer's specification by Mr. Wood Wilson, 2500 Van Buren Street, Wilmington, Delaware.

(10) Wood and Ayliffe, *J. Sci. Instruments*, **12**, 194 (1935).

(11) Obtained from the Parr Instrument Co., Moline, Illinois.

figure for measurement was obtained, the radiation was changed successively to the several monochromatic wave lengths of the mercury arc spectrum and the optic axial angle, $2H$, measured for each wave length.

The principal refractive indices α, β and γ at 25 ± 3° were determined by the immersion method with central illumination, using interference figures as a guide in selecting correctly oriented crystals. Because of their greater constancy, the following series of immersion liquids was employed in preference to the aqueous liquids used in an earlier research.[12]

25° n 5461	Interval between liquids	Constituents
1.410–1.480	0.005	Isoamyl ether-*p*-cymene
1.485–1.660	.005	"Nujol"-α-monobromonaphthalene
1.665–1.750	.005	α-Monobromonaphthalene–methylene iodide
1.755–1.790	.005	Methylene iodide–sulfur
1.795–1.85	.01	Methylene iodide–mixed iodides[13]
1.85–2.01	Variable	Methylene iodide–arsenic–sulfur[14]

The solvent action of the above liquids was only slight in the present case and so caused no inconvenience. Their general usefulness, however, is greater in connection with inorganic crystals than with the more soluble organic ones.

Optical Crystallographic and Melting Point Data

Optical Properties of the Pure Derivatives.—Optical constants of the three crystalline modifications of pure acet-*p*-bromoanilides and of the two corresponding propionic polymorphs are given in Table I.

The present research does not cover the geometric crystallography of the above derivatives. However, literature results for the stable forms of the acetic[5] and propionic[5] (p. 251) derivatives are available in Groth. The crystal system and optical orientations in Table I are from this source. Since orientations are not available for any of the metastable forms, elongations are given as substitutes for the missing data. The emergent bisectrix is included for more precise identification as elongations often vary for different principal sections of the indicatrix. Mügge's $2H$ values for the stable acetic polymorph[5]: 110° 0′ (6708); 110° 55′ (5893) and 111° 48′ (5350) agree approximately with $2H_0$ 108.5° (5461) of Table I but the discrepancy exceeds the errors of the present work. The phase relations of the metastable acetic derivative (II) were studied by Chattaway and Lambert,[3b] who concluded that this polymorph is monotropic or pseudomonotropic.

Constants of the Mixed Crystal System. Application to Analysis.—The series of crystalline products obtained on quenching fused mixtures of acet- and propion-*p*-bromoanilides exhibit continuously varying physical properties over a wide range of compositions, hence may be classed as mixed crystals. The optical properties of this group, particularly optic axial angle and axial dis-

TABLE II

OPTIC AXIAL ANGLE FOR THE SYSTEM PROPION- AND ACET-*p*-BROMOANILIDES USING MONOCHROMATIC LIGHT OF VARIOUS WAVE LENGTHS

Wt. % propionic derivative	Optic axial angle,[a] $2H_a$ (Positive) 4358	5461	5780	6234	6908
100.0	98°	78°	73°	64°	58°
89.4	96°	76°	70°	63°	55°
79.8	94°	70°	63°	54°	44°
70.0	93°	66°	59°	50°	34°
50.2	84°	56°	46°	27°	(22°)[b]
43.1	84°	50°	40°	18°	(32°)
30.1	77°	36°	15°	(33°)	(46°)
21.3	62°	(23°)	(38°)	(45°)	(55°)

[a] Precision ±3°, throughout. [b] Parentheses indicate axial plane ⊥ to position for blue radiation.

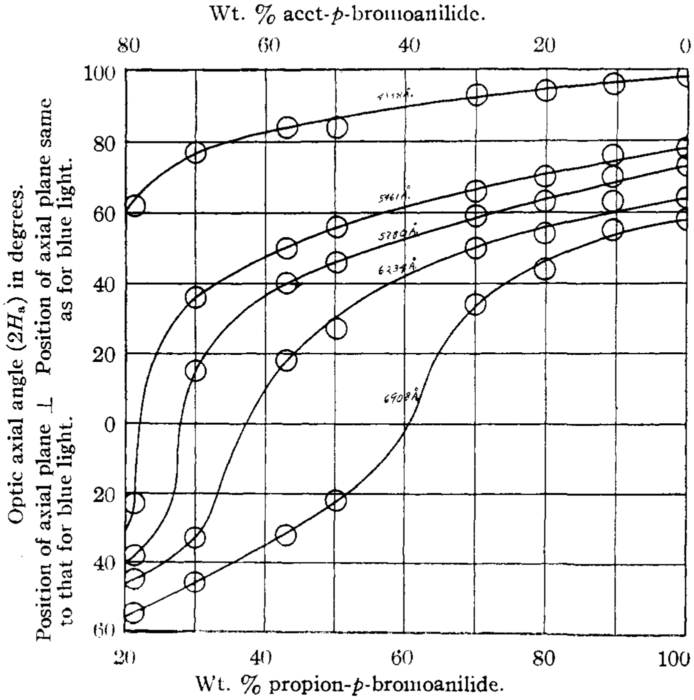

Fig. 1.—Binary system, propion- and acet-*p*-bromoanilides: optic axial angle as a function of composition for several monochromatic radiations of the mercury arc.

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(12) Bryant, THIS JOURNAL, **54**, 3758 (1932).

(13) Merwin, *J. Wash. Acad. Sci.*, **3**, 35 (1913).

(14) Private communication from Dr. Merwin.

persion, show marked changes of magnitude as the composition of the system is varied from 100% down to 20% of the propionic derivative. The lower composition marks the practical limit of the optical method of investigation due to a lack of homogeneity but does not necessarily indicate the termination of the mixed crystal system. Table II contains the optic axial angles of several fused mixtures of known composition measured for five different wave lengths of monochromatic light.

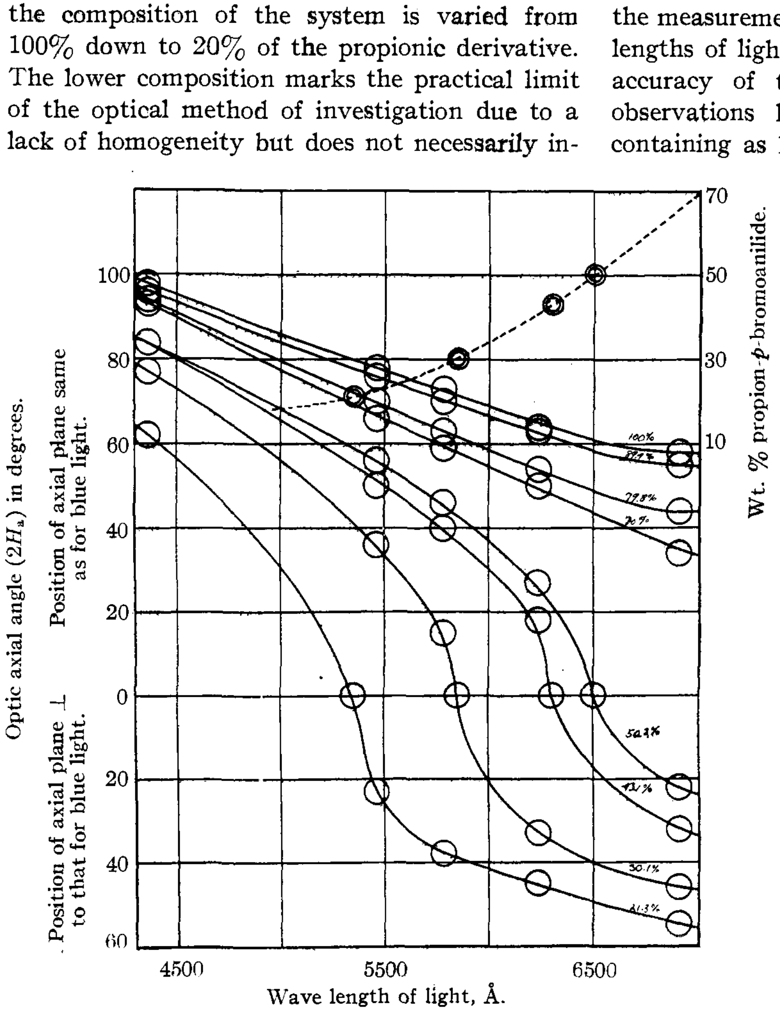

Fig. 2.—Binary system, propion- and acet-*p*-bromoanilides: full curves show optic axial angle as a function of wave length for a series of compositions; broken line curve shows wave length of uniaxiality as a function of composition.

The initial preparation in this tabulation is metastable propion-*p*-bromoanilide, one of the pure components of the binary system.[15] Due to the small size and variable optical quality of the fused preparations, no greater precision than ±3° is claimed for $2H$. This order of precision, however, is quite satisfactory since the rate of change of $2H$ with composition is large. Also the measurement of $2H$ for several different wave lengths of light serves as an added check on the accuracy of the individual results. Although observations have been made upon mixtures containing as little as 20% of the propionic derivative, it is not generally convenient to use Table II for the analysis of mixtures containing less than 30% of this component. The composition can be determined with the best precision in the range 50–100%, but can be ascertained within ±5% over the entire useful range (30–100%). The data are plotted in Figs. 1 and 2. The former is useful in correlating $2H$ and composition for the wave lengths reported. The latter is valuable where other monochromatic light sources have been employed.

In addition to *axial dispersion* which is an outstanding characteristic of the entire system, *crossed axial plane dispersion* is present in crystals containing less than about 60% of the propionic derivative. This form of dispersion involves large displacements of the optic axes such that the substance becomes optically uniaxial for one wave length of light.[16] The characteristic wave length of uniaxiality is an additional criterion of composition as illustrated by the following results obtained with the aid of a calibrated monochromator (Fig. 2).

Wt. % propion-*p*-bromoanilide	Wave length of uniaxiality, Å.
50.2	About 6500
43.1	6300 ± 50
30.1	5850 ± 50
21.3	5350 ± 50

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[15] The pure acetic derivative obtained under the above experimental conditions is the metastable (III) form. Assuming this form is the other pure component of the binary system, the $2H_a$ values in Table II must converge upon $2H_0$ 109° for 0% propion-*p*-bromoanilide. It has not been possible to verify this assumption.

[16] Occasionally, for reasons not clearly understood, a third type of dispersion, "monoclinic" crossed dispersion, is observed in the mixed crystal system but is not, like the other types, a function of composition. Delayed cooling of the melts is believed to favor its occurrence. This third type, when present, probably replaces crossed axial plane dispersion, although the $2H$ results are numerically only slightly affected, the optic axial angle decreasing with a change of the wave length of light to a small finite value instead of zero and finally increasing. The crossed dispersion in mixed *p*-bromoanilides is probably similar to the temporary crossed dispersion observed in mixed crystals of alkali double tartrates by Buckley, *Mineralog Mag.*, **20**, 159 (1924).

The melting points of pure acet- and propion-*p*-bromoanilide and several synthetic mixtures of known composition are given in Table III.

TABLE III

MELTING POINTS OF MIXTURES OF PROPION- AND ACET-*p*-BROMOANILIDES

Wt. % propionic deriv.	M. p., °C. (corr.) ± (0.3°)
100.0	147.0
89.4	147.8
79.8	148.1
70.0	148.8
50.2	151.1
43.1	151.8
30.1	155.1
21.3	157.5
10.0	161.6
0.0	168.8

These data are plotted in Fig. 3, which shows a smooth curve of melting point versus temperature in which there is no minimum indicative of a eutectic. Mixtures of other fatty acid *p*-bromoanilides examined to date have exhibited distinct melting point depression. The present curve is relatively sensitive for analytical purposes in the range below 50% of the propionic derivative but above this composition is not as useful as the optic axial angle plot.

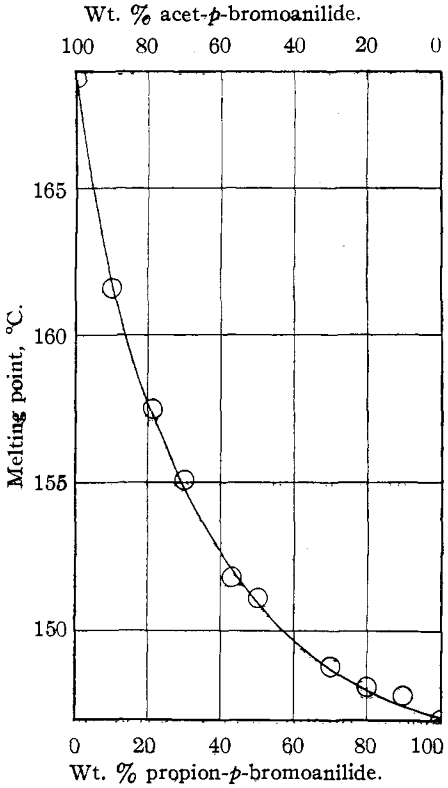

Fig. 3.—Binary system, propion- and acet-*p*-bromoanilides: melting point as a function of composition.

The above tabulated physical data for the *p*-bromoanilide mixed crystal system have been employed to advantage in estimating the ratio of propionic to acetic acid in micro distillates. In this connection identity and composition were determined simultaneously.

Acknowledgment.—The writer wishes to acknowledge the able assistance of Messrs. A. N. Oemler and W. Hawkins by whom the derivatives were prepared.

Summary

1. Optical crystallographic constants of three forms of acet-*p*-bromoanilide and two forms of propion-*p*-bromoanilide have been determined for use as criteria in the identification of the pure derivatives. In addition to the more frequently reported optical constants, acute and obtuse optic axial angles in cedar oil have been measured, and have proved very useful in the above capacity.

2. Optic axial angles in a binary mixed crystal system of acet- and propion-*p*-bromoanilides have been determined for five monochromatic radiations of the mercury arc. Melting points for the same system have also been determined. By means of these physical data, the weight compositions of various binary mixtures can be determined semiquantitatively.

3. Three types of crystal dispersion have been observed in measurable intensity in the above mixed crystal system: axial, crossed axial plane, and "monoclinic" crossed dispersion. The first and second are functions of composition.

WILMINGTON, DELAWARE RECEIVED MARCH 11, 1938