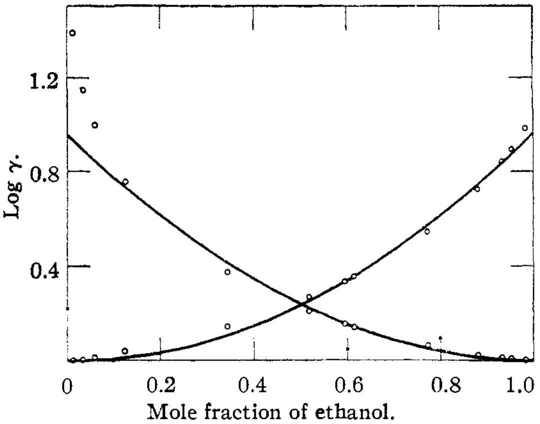

Fig. 6.—Logarithms of activity coefficients at 50°: circles, experimental values; curves, calculated from Van Laar equations.

Figure 6 shows the experimental activity coefficients at 50° compared with curves calculated from the Van Laar equations[20] fitted to the azeotropic composition and pressure. The two-constant Margules equations would give nearly identical curves since the terminal activity coefficients are nearly equal.[20] The agreement is seen to be fairly close except below 0.1 mole fraction where the equations fail to reproduce the rapidly increasing activity coefficient of ethanol. A better fit can be obtained only by using equations with more than two adjustable constants. However, the Van Laar equations would be useful in extending data on other hydrocarbon–alcohol systems, provided the peculiar behavior at low alcohol concentrations were kept in mind.

Summary

Densities of ethanol, isoöctane and of isoöctane–ethanol solutions were measured at 0, 25 and 50°. Equations giving the density of ethanol and isoöctane as a function of temperature are presented. The volume expansion on mixing increases rapidly with temperature.

Static vapor pressures at 0 and 25° and liquid–vapor equilibria at 25 and 50° were determined. Good agreement was obtained between the two sets of measurements at 25°. Satisfactory agreement was also obtained when calculating vapor pressures by means of the Duhem–Margules equation without corrections for imperfection of the vapor.

The excess thermodynamic functions F^E, TS^E and H^M were computed. Activity coefficients were calculated using the Van Laar equation and approximate reproduction of the experimental data were obtained.

PEORIA 5, ILLINOIS RECEIVED NOVEMBER 13, 1947

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(20) H. C. Carlson and A. P. Colburn, *Ind. Eng. Chem.*, **34**, 581 (1942).

[CONTRIBUTION FROM THE THOMPSON LABORATORY OF THE PHILLIPS EXETER ACADEMY]

Melting Point Curves of Optical Isomers

BY CHARLES L. BICKEL AND ALFRED T. PEASLEE, JR.[1]

The problem of the melting points of mixtures of optical isomers was placed on a sound theoretical basis by Roozeboom[2] who showed that three types of melting point curves might be expected. Several of the substances studied[3,4] give the mixed-crystal curve predicted by Roozeboom, a continuous curve joining the melting points of the two optical isomers and a straight line in its simplest form. Most of the compounds investigated[3,4,5] give a curve with two minima and a maximum, indicating the formation of a racemic compound. Ross and Somerville[4] reported that pinene gave the third type of curve, characteristic of a simple mixture and consisting of two parts with a minimum at the point of intersection. However, Timmermans[6] stated that the "dextro" pinene used by Ross and Somerville was a mixture of the two isomers of α-pinene, so that these investigators were working with a ternary mixture and not with optical opposites.

The present study of the dextro and levo forms of β-benzoylhydratropic acid indicates that these optical opposites give a simple mixture. The identity of the isomers appears to be definitely established[7,8,9] so that the question involved in the case of pinene should not be raised in this case.[10] The experimental data for the acids are presented graphically in Fig. 1.

This study has been extended to include the methyl esters of the above acids. Figure 2 indicates that a racemic compound is formed. The behavior of the methyl esters therefore resembles that of most of the acids and esters previously investigated.

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(1) A senior in the Phillips Exeter Academy during the school year, 1947–1948.

(2) Roozeboom, *Z. physik. Chem.*, **28**, 494 (1899).

(3) Adriani, *ibid.*, **33**, 467 (1900).

(4) Ross and Somerville, *J. Chem. Soc.*, 2770 (1926).

(5) Ross, *ibid.*, 718 (1936).

(6) Timmermans, *Bull. soc. chim., Belg.*, **39**, 243 (1930).

(7) Bickel, THIS JOURNAL, **60**, 927 (1938).

(8) Kohler and Bickel, *ibid.*, **63**, 1531 (1941).

(9) Bickel, *ibid.*, **68**, 941 (1946).

(10) Since the submission of this manuscript the observations of Singh and Tewari [*Proc. Indian Acad. Sci.*, **25A**, 389 (1947)] regarding 3-nitro-*p*-toluidinomethylenecamphor have come to our attention. The *d* and *l* isomers of this substance appear to form a simple mixture, the melting point of the eutectic being only 1.8° below the melting point of each pure isomer.

This investigation was assisted by a grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences.

Experimental

A previous paper from this Laboratory[7] adequately described the preparation of the dextro and levo forms of β-benzoylhydratropic acid as well as their methyl esters. Each of these compounds was repeatedly crystallized to ensure purity, the acids from acetone and the esters from a mixture of ether and petroleum ether.. The racemic methyl ester, prepared directly from the hydrogen cyanide addition product of benzylideneacetophenone by the action of methanol and concentrated sulfuric acid, was purified by repeated crystallization from methanol.

Each sample, weighing one-half gram and weighed to the nearest half milligram, was placed in an 8 by 75 mm. Pyrex test-tube which was centered in a sulfuric acid-bath equipped with an efficient motor stirrer and heated by a small burner with chimney. A calibrated tenth-degree thermometer was used, all temperature readings being corrected for emergent stem. The temperature rise of the bath did not exceed one-tenth degree per minute in the region of the melting point of each sample.

Each sample was melted, allowed to solidify, remelted, solidified, and melted at least once more. The original melting points were disregarded in the case of the mixtures. The values for the melting points of each acid mixture agreed to the nearest tenth degree; the tabulated values for the melting points of the ester mixtures are average values, the maximum deviation being one half degree for the mixture containing 90 per cent. of the dextro ester. There was no evidence of racemization or decomposition for either the acids or the esters.

The experimental data are collected below in tabular form.

Acids		Esters	
% Dextro[a]	M. p. in °C.	% Dextro[b]	M. p. in °C.
100	182.1	100	50.3
90	177.8	97	49.2
80	173.3	95	48.8
70	167.1	90	75.7
60	160.2	85	85.9
56	157.3	80	92.5
53	155.5	70	99.7
50	153.9	60	104.3
		55	105.4
		50	106.0

[a] These mixtures were prepared from the dextro and levo acids. The 50% mixture was also realized by using the inactive acid directly. [b] These mixtures were prepared from the dextro and racemic esters. The 50% mixture was also prepared from the dextro and levo esters.

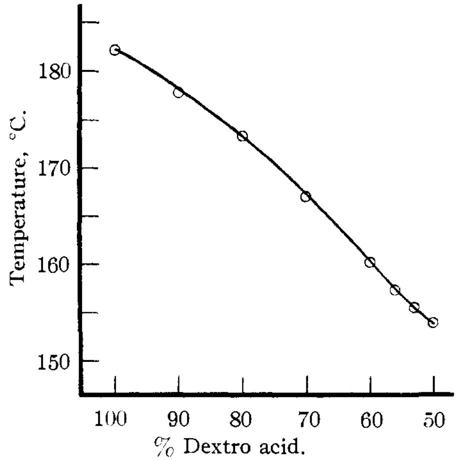

Fig. 1.

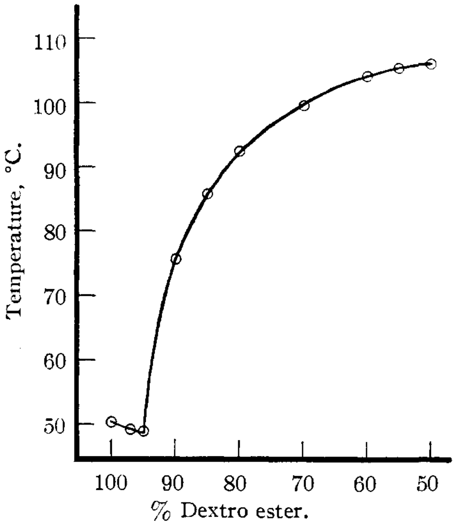

Fig. 2.

The hope of obtaining reliable freezing point curves[11] for these mixtures could not be realized because of marked supercooling of the melts. For example, a five-gram sample of the fifty per cent. acid mixture, melting at 153.9°, showed an initial halt in the freezing point curve at 134° and then at 139° when the experiment was repeated with the same sample. Moreover, the ester mixtures containing a high proportion of either dextro or levo ester remained liquid for several hours in some cases and for several days in others.

Summary

The melting point curve of the dextro and levo forms of β-benzoylhydratropic acid indicates that these isomers give a simple mixture.

The methyl esters of these acids, however, form a racemic compound.

EXETER, NEW HAMPSHIRE RECEIVED JANUARY 2, 1948

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(11) Bickel, THIS JOURNAL, **68**, 866 (1946).