Table II. Constants for Equation 2

R in B(OR)$_3$	*a*	$-b$	*c*	*d*	*S*
CH_3	19.447	1.1743×10^{-1}	-8.1670×10^{-5}	0	8.49×10^{-3}
C_2H_5	19.268	9.6918×10^{-2}	-5.5536×10^{-5}	0	2.81×10^{-2}
C_3H_7	21.470	7.8092×10^{-2}	-1.5798×10^{-4}	8.2359×10^{-7}	3.45×10^{-2}
iso-C_3H_7	17.502	9.3226×10^{-2}	6.1617×10^{-5}	0	3.13×10^{-2}
C_4H_9	23.017	7.1310×10^{-2}	-3.5685×10^{-6}	0	5.04×10^{-2}
iso-C_4H_9	21.362	8.0506×10^{-2}	9.6590×10^{-6}	0	4.60×10^{-2}

the heights read to within ±0.02 cm with an uncalibrated precision cathetometer. At least three or four pairs of readings were taken at any given temperature. The arithmetic mean of the surface tension deduced from each capillary was regarded as the final observation. The difference between the two was in no instance greater than 1%. Densities were taken from a previous work (*3*).

RESULTS AND DISCUSSION

Observed surface tensions were deduced from the usual capillary rise equation for liquids that wet glass and therefore have essentially a zero contact angle,

$$\gamma = hg\rho r/2 \qquad (1)$$

where γ is in dyn cm^{-1}, g is the gravitational constant, ρ is the density, and r is the capillary radius.

The plot of surface tension vs. temperature showed the expected general increase in γ with molecular weight for the unbranched homologs and correspondingly lower γ's for the branched isomers (those of the isopropyl compound being even lower than observations for methyl and ethyl borates). The abnormal amount of curvature shown by the ethyl borate plot above 90°C would seem to confirm the suggestion of partial decomposition unique for this homolog (*5*); a similar anomaly was previously noted in the plot of density vs. temperature (*3*).

Experimental γ's were correlated with temperature by the relationship

$$\gamma = a + b(t - 25) + c(t - 25)^2 + d(t - 25)^3 \qquad (2)$$

where t = °C, and the constants a, b, c, and d were evaluated by polynomial regression analysis.

Observed and calculated γ's are given in Table I along with the per cent deviation as previously defined (*2*). Surface tensions for ethyl borate above 90°C are for the undecomposed compound. These values were calculated from the equation deduced for this homolog from 25–90°C. The last temperature for each borate is the normal boiling point (*2*).

The overall Table I average derivation is ±0.191%. A search of the literature disclosed one report of the γ's of methyl borate at three temperatures between 15-52°C and at four temperatures between 15-64°C for ethyl borate (*4*), and one other investigation of the γ's of propyl and butyl borates at 20°C (*1*). Temperature correlations were not given in either work.

Constants a, b, c, and d for Equation 2 are listed in Table II along with the standard error of estimate, S, as previously defined (*2*).

LITERATURE CITED

(1) Arbuzov, B. A., Vinogradova, V. S., *Compt. Rend. Acad. Sci.* (URSS), **55**, 411 (1947); CA, **41**, 7183i (1947).
(2) Christopher, P. M., Shilman, A., *J. Chem. Eng. Data*, **12**, 333 (1967).
(3) Christopher, P. M., Washington, Jr., H. W., *ibid.*, **14**, 437 (1969).
(4) Etridge, J. J., Sugden, S., *J. Chem. Soc.*, **1928**, p 989.
(5) Webster, S. H., Dennis, L. M., *J. Amer. Chem. Soc.*, **55**, 3233 (1933).

RECEIVED for review February 24, 1971. Accepted July 6, 1971. G. V. G. expresses his thanks to the Esso Research and Engineering Co. for an Esso Foundation Fellowship which provided partial financial assistance during this investigation. This work was abstracted from the MS (Ch.E.) thesis of Gastón V. Guerra, University of Louisville, Louisville, Ky., 1971.

Sound Velocities and Related Properties in Binary Solutions of Aniline

DINKAR D. DESHPANDE,[1] LAXMINARAYAN G. BHATGADDE, SHANTILAL OSWAL, and CHINIVARDH S. PRABHU
Department of Chemistry, Indian Institute of Technology, Powai, Bombay 76, India

In continuation of our work on thermodynamic properties of binary solutions comprising polar and associated liquids (*5–9*), we present in this paper measurements of sound velocities and densities as functions of temperature and composition for solutions of aniline in tetraline, bromobenzene, methanol, *tert*-butanol, pyridine, and tetrahydrofuran. Using Eyring's equation (*11*), we evaluated the free volume in liquids and solutions. The free volume so calculated can be utilized to explain the behavior of liquids and solutions in various ways (*3–5*).

EXPERIMENTAL

Sound Velocity Measurements. The ultrasonic velocities were measured at 3 Mc/sec frequency by using the optical interference method of Hiedemann and Bachem (*14*, *15*). The liquid, contained in an optical glass cell 30 × 30 × 20

---

[1] To whom correspondence should be addressed.

mm and thermostated to ±0.01°C, was excited by an X-cut quartz plate of 1 Mc/sec frequency and driven by a suitable Hartley oscillator at the third harmonic. After a parallel beam of monochromatic light was passed through the cell at right angles to the direction of the propagation of sound waves, the optical fringes obtained were measured by a precision traveling microscope (Soviet EZA.2), reading to 0.001 mm and supplied with a calibrated glass scale with its temperature coefficient. Usually 50–100 fringes were measured to evaluate half wavelength values. This method was rapid and compared in accuracy with that of interferometric methods (*12*, *13*).

The frequency was determined by a superheterodyne beat method by using a Signal Corps BC 221 frequency meter. The wavelength measurement was correct to ±0.05%, and the error in the frequency measurement (1 part in 10^5) was negligible. Therefore, the maximum uncertainty in the velocity measurement was ±0.2%.

Density Measurements. The densities were determined with a Lipkin type (*19*) bicapillary pycnometer with a bulb volume of 16 ml and a capillary diameter of about 0.8 mm. The pycnometer was suspended in an ultrathermostat with a transparent window (supplied by Townson and Mercer, England). The temperature was controlled to ±0.005°C. The liquid level in the two arms of the pycnometer was measured with respect to reference marks by a traveling microscope reading to 0.01 mm.

The pycnometer was calibrated with distilled water and pure benzene. By the constancy of the weight of samples in the pycnometer before and after density determinations, the evaporation of the samples proved negligible owing to the small capillary diameter. The temperature was noted on a NPL-certified thermometer, correct to 0.05°C. All weighings were correct to 0.1 mg. The densities obtained are accurate to 1 part in 10^4.

MATERIALS

All chemicals used were E. Merck. Aniline, methanol, *tert*-butanol, bromobenzene, and pyridine were purified by procedures given by Weissberger (*23*). Aniline was allowed to stand over potassium hydroxide pallets for several weeks and distilled over zinc dust under reduced pressure of 5 mm of Hg. Methanol and *tert*-butanol were purified by repeated fractional distillation over sodium. Bromobenzene, shaken repeatedly with concentrated sulfuric acid until free from thiophene, was washed with aqueous sodium bicarbonate and distilled water, dried over calcium chloride, and fractionally distilled through a column packed with glass helices.

Table VI. Physical Constants and Sound Velocities in Pure Liquids

Liquids		U_L, m sec^{-1}, 20°C	d × 10^3, kg m^{-3}, 25°C	n_D
Aniline	Exptl	1657.0	1.01750	
	Lit	1659^a	1.0175^b	
Bromobenzene	Exptl	1171.1	1.48874	1.5545 (t = 29.5)
	Lit	1170^a	1.4882^b	1.5547^c (t = 29.5)
Tetralin	Exptl	1486.1	0.96321	1.5365 (t = 30.6)
	Lit	1484^d	0.96324^c	1.5367^c (t = 30.6)
Tetrahydrofuran	Exptl	1309.1	0.88436	1.4018 (t = 29.3)
	Lit			
Methanol	Exptl	1120.0	0.78667	
	Lit	1118^d	0.7866^b	
tert-Butanol	Exptl	1142.1	0.78082	1.3814 (t = 30.3)
	Lit		0.78086^c	1.3820 (t = 30.3)
Pyridine	Exptl	1437.2	0.97815	
	Lit	1441^a	0.9778^b	

^{a} Altenberg (*1*). ^{b} Timmermans (*21*, *22*). ^{c} Weissberger (*23*). ^{d} Kuhnkies and Schaaffs (*18*).

Pyridine was purified by allowing it to stand over freshly fused potassium hydroxide for a long time and by repeated fractional distillation. Tetralin (*2*) was treated with concentrated sulfuric acid, washed repeatedly with 10% sodium carbonate solution and distilled water, dried over anhydrous sodium sulfate, and distilled over sodium. Tetrahydrofuran (*20*) was treated with ferrous sulfate to remove traces of peroxide, refluxed with caustic potash and distilled over sodium. Only triple distilled liquids were used for the measurements.

The physical constants and measured sound velocities agreed well with the literature data (Table VI). (Tables I–V have been deposited with the ACS Microfilm Depository Service.) Mixtures were prepared synthetically by weighing appropriate amounts of the pure components in ground glass-stoppered containers.

CALCULATIONS AND RESULTS

The measured values of densities and ultrasonic velocities at various temperatures and compositions are given for the system aniline + bromobenzene in Table VII. (Tables I–V include densities and velocities for the remaining systems.) At each composition the temperature density and temperature velocity data were fitted to an equation $y = a + b(t)$ by a least-squares method, and the density and velocity at 35°C were calculated therefrom. These interpolated values of densities and velocities at 35°C were utilized in the calculation of other properties of solutions (Table XI) as follows: The adiabatic compressibility β_s was obtained as

$$\beta_s = \frac{101.3}{{U_L}^2 \mathrm{d}} \times 10^{-3} \tag{1}$$

The free volume V_f was obtained from Eyring's (*11*) equation as

$$V_f = V(U_g/U_L)^3 \tag{2}$$

Table VII. Density and Sound Velocity in Aniline–Bromobenzene System

X	t, °C	d × 10^3	t, °C	U_L
0.0000	27.5	1.48541	30.0	1136.2
	31.5	1.48007	33.0	1127.8
			36.0	1116.9
			40.0	1105.1
0.1924	35.0	1.39357	31.0	1193.0
	38.5	1.38905	34.6	1181.7
			37.2	1174.6
			40.5	1163.0
0.2977	28.5	1.35552	29.6	1236.7
	32.5	1.35066	33.5	1222.8
	37.0	1.34519	36.3	1213.8
			40.7	1200.0
0.4517	27.8	1.28672	30.5	1293.6
	31.0	1.28308	33.0	1284.9
	34.0	1.27960	37.0	1271.6
	37.0	1.27616	40.3	1261.5
0.5023	32.0	1.25853	28.5	1324.8
	35.0	1.25518	32.0	1311.9
	39.0	1.25067	35.5	1296.9
			40.5	1279.0
0.5552	33.0	1.23272	31.0	1340.0
	36.5	1.22886	34.0	1329.3
	40.0	1.22505	37.0	1318.8
			40.5	1306.8
0.6004	29.7	1.21481	30.7	1363.0
	33.1	1.21125	41.0	1346.4
	36.5	1.20763	41.0	1328.0
0.7085	29.0	1.16331	31.5	1415.0
	32.0	1.16031	35.0	1404.4
	37.0	1.15523	41.2	1381.2
0.8583	30.3	1.08694	32.5	1502.1
	33.5	1.08401	36.5	1488.7
	37.0	1.08069	40.8	1476.5

Experimental data are presented on sound velocities and densities of solutions of aniline in tetraline, bromobenzene, methanol, *tert*-butanol, pyridine, and tetrahydrofuran in the temperature range of 27–43°C and over the whole composition range. From these data the sound velocities and densities are interpolated at 35°C and used to evaluate adiabatic compressibilities, free volumes, excess adiabatic compressibilities, and excess volumes. The accuracies are ±0.20% for velocity measurements, better than 1 part in 10^4 for densities, and ±0.4% for compressibilities.

Table VIII. Molar Heat Capacities of Vapors of Liquids at Zero Pressure

$C_p = a + bT + cT^2 + dT^3$; $(C_v = C_p - R)$

Liquid	a	$b \times 10^2$	$c \times 10^5$	$d \times 10^9$
Aniline	− 2.732	48.212	−24.004	
Bromobenzene	−14.078	42.856	−21.263	
Tetrahydrofuran	−14.267	49.279	−21.409	
Tetralin	−17.585	81.504	−38.589	
tert-Butanol	−33.401	58.325	−23.472	
Pyridine	−18.079	39.715	−18.254	
Methanol[a]	+19.037	9.146	− 1.217	8.033

[a] Hougen et al. (*16*). Note: Four constant equations for methanol and three constant equations for remaining liquid are used.

Sound velocity in the vapor phase was obtained (Jatkar and Laxminarayanan, *17*) from the equation

$$U_g = \left[\frac{C_p}{C_v}\cdot\frac{RT}{M}\left\{1 + \frac{9}{128}\frac{PT_c}{P_cT}\left(1 - 6\frac{T_c^2}{T^2}\right)\right\}\right]^{1/2} \quad (3)$$

In Equation 3 the correction owing to the nonideality of the vapor has been included on the basis of Berthelot's equation of state. The C_p and C_v in the vapor phase were obtained by the method of Dobratz (*10*). These data on heat capacities for vapors are given in Table VIII. For the calculation of V_f according to Equation 2, the additivity of U_g has been assumed in the case of mixtures.

The excess compressibility and excess volume were calculated from Equations 4 and 5, respectively.

$$\beta_s^E = (\beta_s)_{12} - \phi(\beta_s)_1 - (1 - \phi)(\beta_s)_2 \quad (4)$$

$$V^E = V_{12} - XV_1 - (1 - X)V_2 \quad (5)$$

The excess volume and velocity data were fitted to Equations 6 and 7, respectively.

$$V^E = X(1 - X)[A + B(2X - 1) + C(2X - 1)^2 + D(2X - 1)^3] \quad (6)$$

$$U_L = a_0 + a_1X + a_2X^2 + a_3X^3 \quad (7)$$

Table IX. Constants of Excess Volume Equation 6 at 35°C for Six Binary Solutions

System	A	B	C	D
Aniline–bromobenzene	+0.75841	−0.12475	+0.00003	−0.30954
Aniline–tetrahydrofuran	−3.50535	+0.57091	−0.50874	+1.84614
Aniline–Tetralin	+1.52044	−0.43005	+0.27789	+0.56983
Aniline–methanol	−3.78179	+1.02875	−1.36671	+1.91675
Aniline–*tert*-butanol	−2.04659	−0.04347	+0.32103	−0.85543
Aniline–pyridine	−1.73565	−0.57594	+1.53522	−1.95907

Table X. Constants of Sound Velocity Equation 7 at 35°C for Six Binary Solutions

System	a_0	a_1	a_2	a_3
Aniline–bromobenzene	1120.31	+297.01	+ 72.97	+102.84
Aniline–tetrahydrofuran	1230.12	+484.02	−200.53	+ 81.02
Aniline–Tetralin	1425.11	+ 62.40	+ 87.01	+ 15.80
Aniline–methanol	1121.53	+856.23	−376.59	− 31.72
Aniline–*tert*-butanol	1089.85	+419.35	+221.67	−137.46
Aniline–pyridine	1421.69	− 19.30	+419.09	−242.87

Constants A, B, C, and D of Equation 6 and constants a_0, a_1, a_2, and a_3 of Equation 7 are given in Tables IX and X, respectively. All calculations were performed on a Soviet Minsk-2 Computer.

DISCUSSION

For all six systems studied, the excess adiabatic compressibilities and excess volumes (Table XI) always have the same sign. For two systems, aniline–bromobenzene and aniline–Tetralin, the magnitude of excess adiabatic compressibilities is quite small, and as the compressibility measurement has an error of 0.4%, the β_s^E values are insignificant for these two

Table XI. Properties of Aniline Solutions at 35°C

X	$d \times 10^3$	U_L	$\beta_s \times 10^6$	$\beta_s^E \times 10^6$	$V^E \times 10^{-3}$	$V_f \times 10^{-3}$	$V_f \times 10^{-3}$
Aniline–Bromobenzene							
0.0000	1.47539	1120.7	54.7	+0.0	0.0	0.179	0.027
0.1912	1.39357	1180.7	52.2	+0.0	0.142	0.184	
0.2977	1.34766	1218.4	50.6	+0.0	0.171	0.180	
0.4517	1.27846	1278.6	48.5	+0.1	0.193	0.175	
0.5023	1.25517	1299.8	47.8	+0.2	0.189	0.171	
0.5552	1.23052	1325.9	46.8	+0.0	0.185	0.168	
0.6004	1.20922	1348.1	46.1	+0.0	0.175	0.164	
0.7085	1.15724	1403.4	44.5	+0.0	0.139	0.159	
0.8583	1.08260	1494.1	41.9	+0.0	0.069	0.143	
1.0000	1.00880	1594.0	39.5	+0.0	0.0	0.129	

(Continued)

Table XI. *(Continued)*

X	$d \times 10^3$	U_L	$\beta_s \times 10^6$	$\beta^{sE} \times 10^6$	$V^E \times 10^{-3}$	$V_f \times 10^{-3}$	$V_f \times 10^{-3}$
Aniline–Tetrahydrofuran							
0.0000	0.87333	1234.0	76.2	0.0	0.0	0.329	−0.032
0.1912	0.90915	1316.3	64.3	−4.2	−0.696	0.259	
0.4052	0.94135	1397.8	55.1	−5.3	−0.868	0.209	
0.4526	0.94801	1417.4	53.2	−5.4	−0.881	0.198	
0.5136	0.95642	1439.4	51.1	−5.2	−0.895	0.194	
0.6084	0.96805	1469.6	48.5	−4.5	−0.799	0.174	
0.7112	0.97988	1501.9	45.8	−3.5	−0.656	0.161	
0.8092	0.99017	1533.5	43.5	−2.4	−0.454	0.149	
Aniline–Tetralin							
0.0000	0.95535	1426.4	52.1	0.0	0.0	0.137	+0.024
0.1514	0.95938	1436.6	51.2	0.4	0.227	0.143	
0.3999	0.96870	1465.3	48.7	0.5	0.384	0.150	
0.4523	0.97110	1472.5	48.1	0.5	0.392	0.147	
0.6059	0.97937	1496.7	46.2	0.4	0.343	0.145	
0.7078	0.98560	1518.6	44.7	0.3	0.297	0.142	
0.7989	0.99183	1536.9	43.2	0.3	0.238	0.139	
Aniline–Methanol							
0.0000	0.77713	1069.0	114.1	0.0	0.0	1.004	−0.251
0.2050	0.87612	1280.2	70.5	−16.3	−0.856	0.548	
0.3996	0.93061	1400.7	55.5	−14.0	−0.997	0.376	
0.4361	0.93778	1418.1	53.7	−13.1	−0.947	0.352	
0.5050	0.95144	1455.6	50.3	−12.0	−0.940	0.311	
0.5441	0.95836	1471.0	48.8	−11.0	−0.922	0.290	
0.7049	0.98139	1526.8	44.3	− 7.0	−0.722	0.221	
0.7975	0.99147	1548.7	42.6	− 4.5	0.523	0.189	
Aniline–*tert*-Butanol							
0.0000	0.77070	1076.8	113.4	0.0	0.0	0.567	−0.097
0.1920	0.81722	1177.6	87.4	−10.3	−0.268	0.407	
0.3098	0.84599	1236.6	78.3	−12.8	−0.403	0.339	
0.4030	0.86876	1287.0	70.4	−13.9	−0.483	0.289	
0.4547	0.88143	1312.6	66.7	−13.8	−0.523	0.271	
0.5761	0.91021	1379.0	58.5	−13.0	−0.488	0.222	
0.6523	0.92844	1419.5	54.1	−11.7	−0.470	0.202	
0.7600	0.95377	1476.3	48.7	− 9.1	−0.383	0.174	
0.8570	0.97647	1525.6	44.6	− 5.8	−0.273	0.153	
Aniline–Pyridine							
0.0000	0.96820	1343.0	58.0	0.0	0.0	0.233	−0.003
0.2713	0.98360	1442.4	49.5	−3.0	−0.291	0.193	
0.4218	0.99171	1471.3	47.2	−2.5	−0.449	0.180	
0.4533	0.99292	1474.9	46.9	−2.2	−0.443	0.177	
0.5066	0.99480	1487.6	46.0	−2.1	−0.420	0.171	
0.5550	0.99651	1497.8	45.3	−1.9	−0.401	0.166	
0.6005	0.99800	1510.4	44.5	−1.9	−0.375	0.160	
0.8164	1.00402	1553.4	41.8	−0.8	−0.176	0.143	

systems but have the same positive sign as that of the excess volume.

Further, one can define excess free volume as

$$V_f^E = (V_f)_{12} - (V_f)_{12}^{\text{ideal}}$$

$$= (V_f)_{12} - [XV_1 + (1 - X)V_2]\left[\frac{XU_{g1} + (1 - X)U_{g2}}{XU_{L1} + (1 - X)U_{L2}}\right]^3 \qquad (8)$$

Since the magnitude of the free volumes is small, the excess free volume as defined above has not been evaluated. For comparison of signs of excess functions β_s^E and V^E, the following free volume difference was obtained:

$$\Delta V_f = (V_f)_{12} - X(V_f)_1 - (1 - X)(V_f)_2 \qquad (9)$$

The free volume differences ΔV_f obtained for these systems have the same sign as that of excess volume (Table XI). The usefulness of the free volume data in explaining the hindered rotation will be published elsewhere (*4*).

NOMENCLATURE

a_0, a_1, a_2, a_3 = constants of Equation 7
A, B, C, D = constants of Equation 6
C_p, C_v = heat capacities at constant pressure and constant volume in vapor phase, J kg^{-1} mol^{-1}
d = density, kg m^{-3}
M = molecular weight
n_D = refractive index
P = atmospheric pressure, atm
R = gas constant
T = absolute temperature
t = temperature, °C
X = mole fraction of aniline
U = sound velocity, m sec^{-1}
V = molar volume, m^3 kg^{-1} mol^{-1}
V_f = free volume, m^3 kg^{-1} mol^{-1}
ΔV_f = free volume difference, m^3 kg^{-1} mol^{-1}
β_s = adiabatic compressibility, atm^{-1}
ϕ = volume fraction

Subscripts

1 = first component
2 = second component
12 = mixture of 1 and 2
c = critical constants
g = gas phase
L = liquid phase

Superscripts

E = excess function

LITERATURE CITED

(1) Altenberg, K., *Z. Physik. Chem.*, **216**, 139 (1961).
(2) Bass, K. C., *J. Chem. Soc.*, **1964**, p 3498.
(3) Bhatgadde, L. G., PhD thesis, Indian Institute of Technology, Bombay, India, 1969.
(4) Deshpande, D. D., Bhatgadde, L. G., *Aust. J. Chem.*, in press (1971).
(5) Deshpande, D. D., Bhatgadde, L. G , *J. Phys. Chem.*, **72**, 261 (1968).
(6) Deshpande, D. D., Pandya, M. V., *Trans. Faraday Soc.*, **61**, 1858 (1965).
(7) Deshpande, D. D., Pandya, M. V., *ibid.*, **63**, 2149 (1967).
(8) Deshpande, D. D., Pandya, M. V., *ibid.*, p 2346.
(9) Deshpande, D. D., Pandya, M. V., *ibid.*, **65**, 1456 (1969).
(10) Dobratz, C. S., *Ind. Eng. Chem.*, **33**, 759 (1941).
(11) Eyring, H., Hirschfelder, J. O., *J. Phys. Chem.*, **41**, 249 (1937).
(12) Fort, R. J., Moore, W. R., *Trans. Faraday Soc.*, **61**, 2102 (1965).
(13) Guecker, F. T., Chernick, C. L., Chowdhury, P. R., *Proc. Nat. Acad. Sci.* (U.S.), **55**, 12 (1966).
(14) Hiedemann, E., Bachem, Ch., *Z. Physik.*, **91**, 418 (1934).
(15) Hiedemann, E., Bachem, Ch., *ibid.*, **94**, 68 (1935).
(16) Hougen, O. A., Watson, K. H., Ragatz, R. A., "Chemical Progress Principles," Vol 1, Wiley, New York, N.Y., 1959.
(17) Jatkar, S. K. K., Laxminarayanan, O., *J. Ind. Inst. Sci.* (Bangalore), **A-28**, 1 (1946).
(18) Kuhnkies, R., Schaaffs, W., *Acustica*, **13**, 408 (1963).
(19) Lipkin, M. R., Davison, J. T., Harvey, W. T., Kurtz, S. S., *Ind. Eng. Chem., Anal. Ed.*, **16**, 55 (1944).
(20) Sannigrahi, A. B., Chandra, A. K., *J. Phys. Chem.*, **67**, 1105 (1963).
(21) Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds," Vol 1, Elsevier, Amsterdam, The Netherlands, 1950.
(22) Timmermans, J., *ibid.*, Vol 2, 1965.
(23) Weissberger, A., "Techniques of Organic Chemistry," Vol 7, Interscience, New York, N.Y., 1959, pp 333, 349, 424, 441, 445.

RECEIVED for review March 8, 1971. Accepted June 16, 1971. Two authors, L. G. B. and S. L. O., express their thanks to CSIR for junior research fellowships. Tables I–V will appear following these pages in the microfilm edition of this volume of the Journal. Single copies may be obtained from the Reprint Department, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D.C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

Binary Freezing-Point Behavior of Methyl and Ethyl Esters of Positional and Geometric Isomers of Octadecenoic Acid

AUGUST V. BAILEY,[1] JAMES A. HARRIS, and EVALD L. SKAU
Southern Regional Research Laboratory, New Orleans, La. 70119

Mutual solubilities have been obtained on both the methyl and ethyl esters of geometric isomers of two octadecenoic acids. Binary systems investigated were methyl petroselinate–methyl petroselaidate, methyl oleate–ethyl elaidate, ethyl petroselinate–ethyl petroselaidate, ethyl oleate–ethyl elaidate, methyl oleate–methyl petroselinate, methyl elaidate–methyl petroselaidate, ethyl oleate–ethyl petroselaidate, and ethyl oleate–ethyl petroselinate. Simple eutectic systems were obtained for all combinations of the cis, trans, and positional isomers investigated. No polymorphism was observed in either the pure compounds or the binary mixtures.

Recently, special interest has been attached to the preparation and purification of closely related mono and dienoic acids and esters in biological studies. Whereas the mutual solubilities of the methyl and ethyl esters of the saturated acids have been studied by numerous investigators, little information is available on the unsaturated acids and esters. In our continuing investigations of the solubilities of fatty acids and fatty acid derivatives (*1-5*, *7*), we have prepared geometric isomers of the Δ6 and Δ9 octadecenoic acids. Binary freezing-point behavior of the methyl and ethyl esters of these acids is reported.

EXPERIMENTAL

The pure acids used in the preparation of the esters were recrystallized materials prepared from the fractionally distilled methyl esters. The trans isomers of the acids were prepared by the procedure of Mack and Bickford (*8*) which involves shaking the acid in a separatory funnel in the presence of a mixture of sodium nitrite and dilute nitric acid followed by solvent crystallization of the isomerized acid. The methyl or ethyl ester was prepared by refluxing the pure acid in an excess of the anhydrous alcohol in the presence of catalytic amounts of toluene sulfonic acid followed by solvent crystallization.

The purity of the esters and their freezing points were determined using the method of heating curves and apparatus described by Skau (*10*). The heating curves were run on approximately 0.5-gram samples in a sealed glass tube fitted with a thermocouple well. The sample tube was suspended in a copper block also fitted with a thermocouple well. The entire assembly was cradled in an unsilvered Dewar flask using liquid nitrogen as a coolant. The temperature of the solidified sample was risen at a rate of approximately 0.2°C/min. Both the block and sample temperatures were moni-

---

[1] To whom correspondence should be addressed.