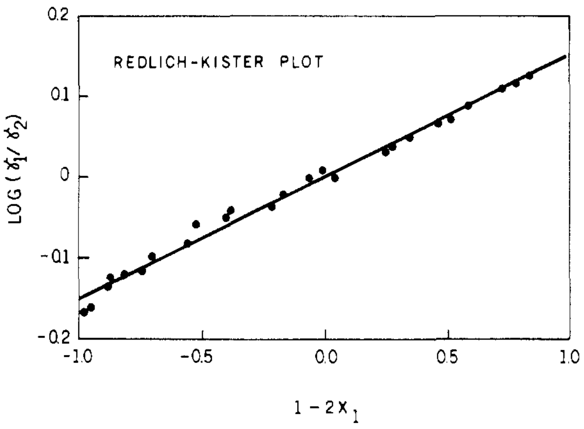

Figure 3. Test of eq 4.

Acknowledgment

Yehudit Reizner and Moshe Golden helped in the experimental and numerical calculations.

Glossary

α, β, δ	constants
B_{ii}, B_{ij}	virial coefficients
ΔG^E	excess of the Gibbs function
n	number of experimental points
P	total pressure, mmHg
$P_i°$	vapor pressure of pure component, mmHg
R	gas constant, 82.06 cm^3/(g·mol·K)
rmsd	root-mean-square deviation $[\sum(T_{exptl} - T_{calcd})^2/n]^{1/2}$
t, T	temperature, °C, K
v_i^L	molar volume of pure liquid i, mL/mol
x_i, y_i	molar fraction of component i in the liquid and vapor phases
γ_i	activity coefficient of component i

Subscripts

calcd	calculated
exptl	experimental
i, j	components i, j

Registry No. Propyl bromide, 106-94-5; vinyl acetate, 108-05-4; methyl methacrylate, 80-62-6.

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Vapor-Liquid Equilibria at 760 mmHg in the Systems Methyl Acetate-Propyl Bromide, Methyl Acetate-Toluene, and Methyl Methacrylate-Toluene

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Vapor-liquid equilibria for the title systems have been determined at 760 mmHg. The three systems exhibit positive deviations from ideal behavior. The boiling points were well correlated with the composition of the liquid phase.

The present work is part of our program for determining VLE data for organic systems in which one of the components is a bromide. No literature data are available for comparison purposes.

Experimental Section

Purity of Materials. Propyl bromide (99.4+%) and methyl acetate (99.2+%) were supplied by Merck, analytical grade methyl methacrylate (99.4+%) was supplied by Fluka, and toluene (99.6+%) was supplied by Frutarom. The reagents were used without further purification after gas chromatography analysis failed to show any significant impurities (none higher than 0.2 mol %). Properties of the components appear in Table I.

Table I. Physical Properties of Pure Components

compound	refractive index (25 °C)	normal bp, °C
propyl bromide	1.4320^a	70.55^a
	1.4317^b	70.80^c
methyl acetate	1.3588^a	56.94^a
	1.3589^b	56.94^b
methyl methacrylate	1.4118^a	100.4^a
	1.4120^c	100.3^d
toluene	1.4926^a	110.70^a
	1.4941^b	110.80^b

^{a}This work. ^{b}Reference *8*. ^{c}Reference *9*. ^{d}Reference *10*.

Apparatus and Procedure. An all-glass-modified Dvorak-Boublik recirculation still (*1*) was used in the equilibrium determinations. The experimental details have been described in previous publications (*2*). In order to reduce the polymerization of methyl methacrylate, up to 0.2 wt % of hydroquinone monomethyl ether was added to the original reagent. All analyses were carried out by gas chromatography on a Packard-Becker 417 chromatograph provided with thermal conductivity detector and an Spectra Physics Model SP 4290 electronic integrator. The column was 200 cm long and 0.2 cm in diameter and packed with 20% OV-17. Temperatures were column, 90 °C (120 °C for methyl acetate-toluene); injector, 220 °C; and detector, 230 °C. Very good separation was achieved with helium as the gas carrier, and calibration analyses were carried

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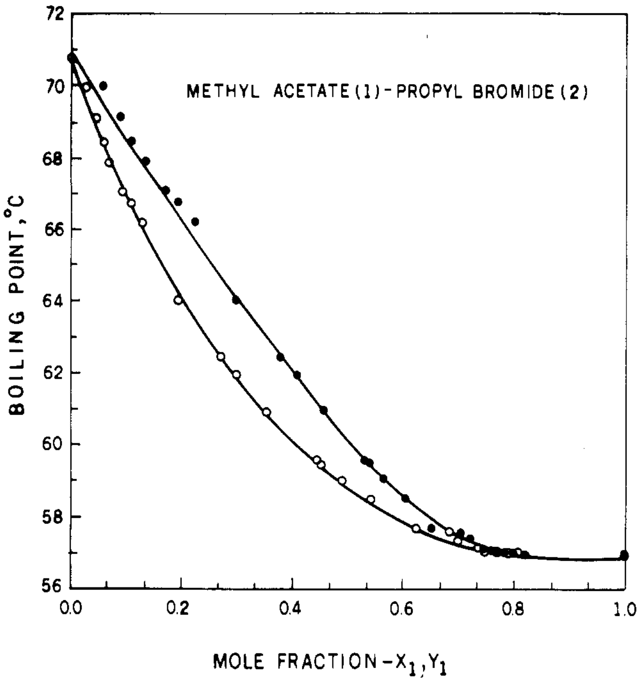

Figure 1. Boiling point diagram for the system methyl acetate (1)-propyl bromide (2).

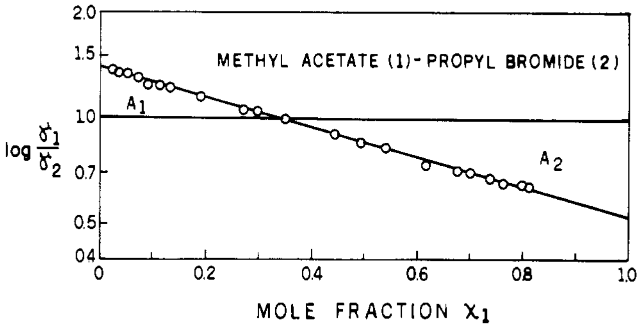

Figure 2. Activity coefficients for the system methyl acetate (1)-propyl bromide (2).

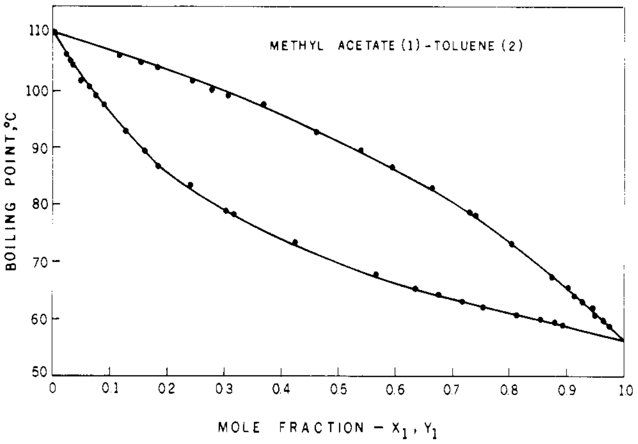

Figure 3. Boiling point diagram for the system methyl acetate (1)-toluene (2).

Table II. Experimental Vapor-Liquid Equilibria Data for Methyl Acetate (1)-Propyl Bromide (2) at 760 mmHg

temp, °C	x_1	y_1	γ_1	γ_2
70.00	0.026	0.054	1.3693	1.0014
69.14	0.044	0.088	1.3536	1.0088
68.48	0.057	0.110	1.3328	1.0175
67.92	0.071	0.134	1.3260	1.0248
67.07	0.093	0.169	1.3108	1.0343
66.75	0.108	0.192	1.2951	1.0329
66.23	0.129	0.223	1.2799	1.0339
64.00	0.191	0.296	1.2309	1.0852
62.46	0.270	0.380	1.1741	1.1133
61.97	0.302	0.409	1.1631	1.1213
60.95	0.353	0.456	1.1316	1.1544
59.61	0.444	0.531	1.0945	1.2104
59.52	0.451	0.539	1.0970	1.2085
59.05	0.491	0.566	1.0746	1.2464
58.52	0.543	0.604	1.0552	1.2892
57.71	0.622	0.653	1.0262	1.3909
57.59	0.680	0.703	1.0115	1.4246
57.40	0.700	0.719	1.0114	1.4469
57.15	0.735	0.745	1.0057	1.5020
57.09	0.752	0.760	1.0075	1.5137
57.07	0.766	0.772	1.0033	1.5220
57.05	0.787	0.791	1.0026	1.5359
57.03	0.797	0.799	0.9960	1.5436
57.00	0.807	0.815	1.0123	1.5705

Table III. Experimental Vapor-Liquid Equilibria Data for Methyl Acetate (1)-Toluene (2) at 760 mmHg

temp, °C	x_1	y_1	γ_1	γ_2
106.56	0.018	0.115	1.5950	1.0083
105.38	0.024	0.149	1.5930	1.0085
104.43	0.030	0.178	1.5565	1.0068
101.78	0.044	0.241	1.5300	1.0177
100.84	0.051	0.269	1.5070	1.0147
99.32	0.060	0.304	1.5019	1.0197
97.18	0.078	0.365	1.4619	1.0106
93.00	0.113	0.459	1.4097	1.0156
89.41	0.149	0.534	1.3648	1.0194
86.79	0.185	0.591	1.3040	1.0153
83.24	0.237	0.658	1.2478	1.0175
79.02	0.301	0.726	1.2195	1.0241
78.54	0.313	0.731	1.1970	1.0397
73.55	0.418	0.803	1.1380	1.0676
68.12	0.562	0.869	1.0791	1.1458
65.75	0.632	0.900	1.0697	1.1359
64.82	0.670	0.910	1.0506	1.1803
63.24	0.713	0.924	1.0541	1.2161
62.47	0.752	0.935	1.0366	1.2393
61.33	0.808	0.947	1.0138	1.3633
60.28	0.853	0.959	1.0063	1.4342
59.72	0.877	0.967	1.0052	1.4099
59.37	0.888	0.969	1.0063	1.4744
57.85	0.950	0.986	1.0066	1.5828

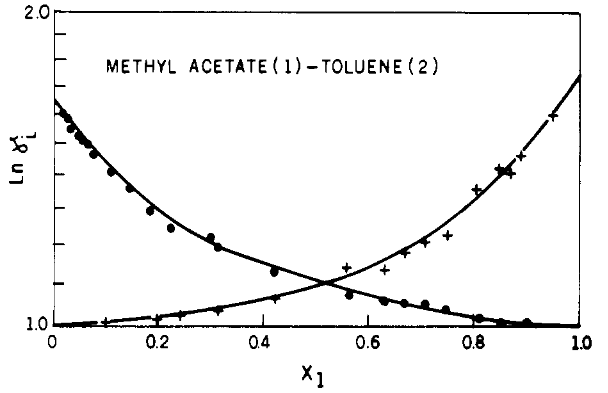

Figure 4. Activity coefficients for the system methyl acetate (1)-toluene (2).

out to convert the peak area ratio to composition of the sample. Concentration measurements were accurate to better than ±1%. The accuracy in determination of pressure and temperature was $\Delta P = \pm 2$ mmHg and $\Delta T = \pm 0.02$ °C.

Results

The temperature-concentration measurements at 760 mmHg are reported in Tables II-IV and Figures 1-6. The boiling point diagram of the binary methyl acetate-propyl bromide becomes very flat at methyl concentrations above 0.8 M, and

Table IV. Experimental Vapor-Liquid Equilibria Data for Methyl Methacrylate (1)-Toluene (2) at 760 mmHg

temp, °C	x_1	y_1	γ_1	γ_2
110.08	0.038	0.054	1.1432	0.9982
108.62	0.121	0.165	1.1404	1.0038
108.20	0.142	0.191	1.1377	1.0081
107.95	0.164	0.218	1.1319	1.0071
107.72	0.170	0.224	1.1290	1.0130
106.82	0.230	0.293	1.1201	1.0203
106.58	0.260	0.332	1.1282	1.0100
106.07	0.294	0.369	1.1244	1.0146
105.61	0.329	0.403	1.1113	1.0232
104.58	0.437	0.508	1.0857	1.0356
104.00	0.507	0.570	1.0661	1.0509
103.54	0.571	0.630	1.0596	1.0534
102.88	0.650	0.692	1.0412	1.0958
102.70	0.679	0.717	1.0382	1.1037
102.64	0.728	0.745	1.0078	1.1137
102.02	0.781	0.808	1.0368	1.1203
101.81	0.795	0.821	1.0411	1.1227
101.65	0.828	0.850	1.0396	1.1269
101.69	0.845	0.864	1.0343	1.1326
101.33	0.866	0.883	1.0421	1.1391

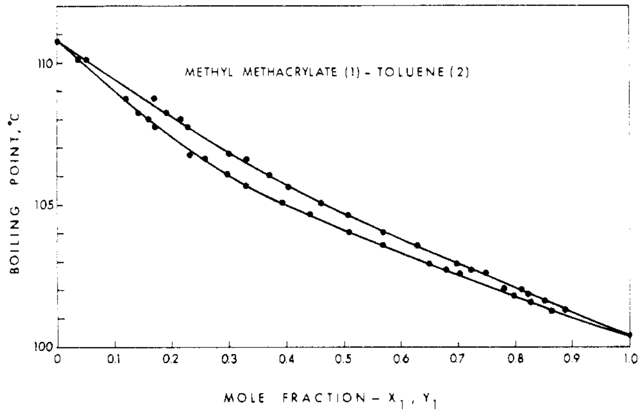

Figure 5. Boiling point diagram for the system methyl methacrylate (1)–toluene (2).

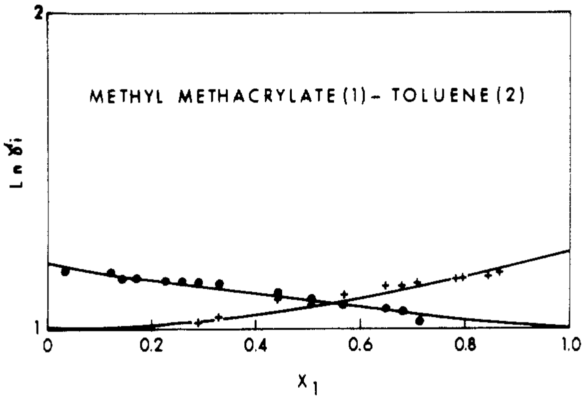

Figure 6. Activity coefficients for the system methyl methacrylate (1)–toluene (2).

there is the possibility of an azeotrope at higher concentrations. The latter could not be determined experimentally because the difference in concentration between the two phases was of the order of the analytical error.

The activity coefficients were calculated from the equations

$$\ln \gamma_1 = \ln (Py_1/P^\circ_1 x_1) + (B_{11} - v^L_1)(P - P^\circ_1)/RT + P(1 - y_1)^2\delta_{12}/RT \quad (1)$$

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \quad (2)$$

Table V. Antoine Constants

	α_i	β_i	δ_i
propyl bromide[a]	6.910 65	1194.889	225.51
methyl acetate[a]	7.061 31	1156.43	219.69
methyl methacrylate[b]	7.109 00	1387.86	226.15
toluene[a]	6.954 64	1344.80	219.482

[a] Reference *8*. [b] Reference *11*.

Table VI. Redlich-Kister Constants, Eq 5

system	*B*	*C*	*D*	*E*	R^2
methyl acetate (1)–propyl bromide (2)	0.229	–0.151	0.037	0.293	0.998
methyl acetate (1)–toluene (2)	0.195	0	0	0	0.995
	0.191	0.018	0.035	0	0.998
methyl methacrylate (1)–toluene (2)	0.065	0.014	–0.027	–0.030	0.993

The last two terms contributed less than 2% to the activity coefficient, and their influence was important only at very dilute concentrations.

Vapor pressures of the pure components, P°_i, were calculated according to Antoine's equation:

$$\log P^\circ_i = \alpha_i - \beta_i/(t + \delta_i) \quad (3)$$

where the constants appear in Table V. The molar virial coefficients B_{11}, B_{22}, and B_{12} were estimated by the method of Tsonopoulos (*3*, *4*) using the parameters suggested by the author.

The activity coefficients reported in Tables II–IV for the two binaries methyl acetate–toluene and methyl methacrylate–toluene are thermodynamically consistent by the area and Herington (*5*) tests and exhibit positive deviations from Raoult's law. The binary system methyl acetate–propyl bromide shows positive deviations from Raoult's law but clearly does not satisfy the area consistency test. One possibility for the inconsistency is the presence of a significant heat of mixing effect, in which case we can apply the Herington (*7*) consistency test. According to Herington (*5*) a set of activity coefficients is consistent if the condition $|D - J| < 10$ is met, where *D* and *J* have the following meaning:

$$D = 100(A_1 - A_2)/(A_1 + A_2)$$
$$J = 150(T_{\max} - T_{\min})/T_{\min} \quad (4)$$

From the data of Table III and Figure 2 we obtain $D = 14.06$ and $J = 6.4$; hence the data may be considered thermodynamically consistent.

Activity coefficients of the three binaries were correlated by the Redlich–Kister expansion (*6*):

$$\log \gamma_1/\gamma_2 = B(x_2 - x_1) + C(6x_1x_2 - 1) + D(x_2 - x_1)(1 - 8x_1x_2) + E(x_2 - x_1)^2(2x_1x_2 - 1) \quad (5)$$

The pertinent parameters and coefficients of determination R^2 appear in Table VI.

It is interesting to note that the binary system methyl acetate–propyl bromide can also be represented by the simple equation

$$\log \gamma_1/\gamma_2 = 0.144 - 0.4228x_1 \quad (6)$$

Boiling points of the binary system were correlated by the equation suggested by Wisniak and Tamir (*7*):

$$T = x_1T_1 + x_2T_2 + x_1x_2[C_0 + C_1(x_1 - x_2) + C_2(x_1 - x_2)^2 + \ldots] \quad (7)$$

An optimization technique yielded the values for the constants reported in Table VII.

Table VII. Boiling Point Constants, Eq 7

system	C_0	C_1	C_2	C_3	rmsd
methyl acetate (1)–propyl bromide (2)	–19.719	5.5406			0.14
methyl acetate (1)–toluene (2)	–53.413	30.334	–31.187	30.197	0.37
methyl methacrylate (1)–toluene (2)	–6.2089	4.1396			0.68

Acknowledgment

Yehudit Reizner and Moshe Golden helped in the experimental and numerical calculations.

Glossary

α, β, δ	Antoine constants
B_{ii}, B_{ij}	molar virial coefficients
n	number of experimental points
P	total pressure, mmHg
P°_i	vapor pressure of pure component, mmHg
R	molar gas constant, 62 363.7 cm^3 mmHg $mol^{-1} \cdot K^{-1}$
rmsd	root-mean-square deviation $[\sum(T_{exptl} - T_{calcd})^2/n]^{1/2}$
t, T	temperature, °C, K
v^L_i	molar volume of pure liquid i, mL/mol
x_i, y_i	molar fraction of component i in the liquid and vapor phases
γ_i	activity coefficient of component i

Subscripts

calcd	calculated
exptl	experimental
i, j	component i, j

Registry No. MeOAc, 79-20-9; PrBr, 106-94-5; PhMe, 108-88-3; methyl methacrylate, 80-62-6.

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Ultrasonic Velocity in and Adiabatic Compressibility for Some Fluorocarbon Liquid Mixtures

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Ultrasonic velocity, c, and adiabatic compressibility, β_s, have been determined at 298.16 K for six fluorocarbon binary liquid mixtures over the entire composition range. A very low value of ultrasonic velocity in liquids finds practical application in the ultrasound light modulator system. In the liquid mixtures studied useful ultrasonic velocities in the range 477–714 ms^{-1} were obtained at ambient temperature. This study reveals the possibility of obtaining any desired ultrasonic velocity in the above range by mixing two distinctive fluorocarbon liquids in a definite proportion. For the binary systems studied, the excess adiabatic compressibility ($\Delta\beta_s$) at equimolar mixture in general shows a decreasing trend with the increase in difference of boiling points.

Introduction

Liquids with a very low ultrasound propagation velocity below 900 ms^{-1} find extensive applications in sound lenses, cavity resonators, and of late in ultrasound light modulator systems. A very low ultrasound propagation velocity was recently investigated by the authors (*1*) in liquid perfluoropentanes (Flutec PP50) as 477 ms^{-1} at 298.16 K. It is the lowest velocity ever measured in a liquid at ambient temperature. Further, it is very useful to have liquids or solutions with a wide range of low ultrasonic velocities for practical reasons. This paper presents the ultrasonic velocity c and adiabatic compressibility β_s of six different fluorocarbon liquid mixtures at room temperature.

Table I. Comparison of Density and Ultrasonic Velocity in Certain Standard Liquids at 298.16 K

	$\rho \times 10^{-3}$, kg m^{-3}		c, m s^{-1}	
liquid	this work	lit.	this work	lit.
water	0.997_2	0.9970[a]	1496	1496.5[a]
benzene	0.873_4	0.8736[b]	1298	1299.1[b]
carbon tetrachloride	1.584_1	1.5844[b]	922	921.2[b]

[a] Reference *3*. [b] Reference *4*.

Experimental Section

The fluorocarbon liquids, perfluoropentanes, C_5F_{12} (Flutec PP50); perfluorohexanes, C_6F_{14} (Flutec PP1); perfluoromethylcyclohexanes, C_7F_{14} (Flutec PP2); and perfluorodecalin isomers, $C_{10}F_{18}$ (Flutec PP5), which are commercially available from ISC Chemicals Ltd. (UK), have been used in these studies. The trade names of the respective liquids are given in parentheses. The normal (1 atm) boiling points of these liquids are 302.16, 330.16, 349.16, and 415.16 K and respectively agree with the published values (*2*).

The ultrasonic velocities were determined with a single-crystal variable-path interferometer. The values were measured at 1-MHz frequency to an accuracy of ±0.1%. The temperature of the experimental liquid was controlled to within ±0.1 K by using MLW thermostat U10. The density ρ of the experimental

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