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

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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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Table II. Experimental Values of Ultrasonic Velocity in and Adiabatic Compressibility for Various Systems of Fluorocarbon Liquids at 298.16 K

X_1	c, ms^{-1}	$\rho \times 10^3$, kg m^{-3}	β_s, TPa^{-1}
	Flutec PP1–Flutec PP50		
0	477	1.6081	2734
9.04	474	1.6190	2749
18.28	472	1.6300	2754
37.37	492	1.6456	2509
47.23	498	1.6540	2438
57.31	510	1.6627	2312
78.16	522	1.6806	2183
100	548	1.6890	1972
	Flutec PP2–Flutec PP50		
0	477	1.6081	2734
18.58	511	1.6500	2321
37.84	536	1.6871	2063
47.71	547	1.7072	1958
57.79	554	1.7248	1889
78.50	589	1.7542	1644
100	619	1.7841	1463
	Flutec PP5–Flutec PP50		
0	477	1.6081	2734
15.71	532.6	1.6936	2081
33.22	586.4	1.7573	1655
42.73	611.8	1.7940	1489
52.79	638.5	1.8213	1348
74.29	678	1.8743	1161
100	714	1.9242	1020
	Flutec PP2–Flutec PP1		
0	548	1.6890	1972
20.32	557.8	1.7146	1874
40.47	569	1.7364	1779
50.49	573	1.7480	1743
60.46	581.6	1.7561	1684
80.37	599.8	1.7721	1569
100	619	1.7841	1463
	Flutec PP5–Flutec PP1		
0	548	1.6890	1972
17.24	566.2	1.7568	1775
35.72	600	1.8024	1532
45.43	614.1	1.8300	1456
55.55	636.8	1.8511	1331
76.90	666.8	1.8909	1190
100	714.0	1.9242	1020
	Flutec PP5–Flutec PP2		
0	619	1.7841	1463
8.32	602.2	1.8080	1525
17.29	596.4	1.8268	1539
35.26	621.0	1.8571	1396
44.95	635.5	1.8735	1322
55.05	647.8	1.8872	1263
65.58	668.0	1.9000	1180
76.54	688.8	1.9134	1102
88.02	700.5	1.9220	1060
100	714.0	1.9242	1020

liquid was measured by use of a specific gravity bottle to an accuracy of ±0.05%.

With a view to establishing the accuracy of the authors' method, the values of ultrasonic velocity, c, and density, ρ, in certain standard liquids like water, benzene, and carbon tetrachloride were determined and the results were compared in Table I with the literature values (*3*, *4*). There is fairly good agreement between the values.

Results

The experimental values of c, ρ, and β_s at various mole fractions X_1 in six different fluorocarbon binary mixtures have been presented in Table II. The adiabatic compressibility β_s was calculated by using the relation

$$\beta_s = c^{-2}\rho^{-1} \tag{1}$$

Table III. Excess Properties of Equimolar Liquid Mixtures at 298.16 K

mixture	Δc, ms^{-1}	$\Delta\beta_s$, TPa^{-1}	diff in bp, K
PP1–PP50	−12.5	+80	28
PP2–PP50	+3.5	−150	47
PP5–PP50	+35.0	−480	113
PP2–PP1	−9.5	+30	19
PP5–PP1	−9.0	−98	85
PP5–PP2	−22.0	+50	66

Table IV. Concentration Coefficient of Compressibility and Density in Six Fluorocarbon Binary Liquids at Equimolar Mixture

mixture	$(1/\beta_s)(d\beta_s/dX_1)$	$(1/\rho)(d\rho/dX_1)$	% contribn[a]
PP1–PP50	0.516	0.052	9.15
PP2–PP50	0.352	0.103	22.63
PP5–PP50	1.046	0.149	12.46
PP2–PP1	0.338	0.046	11.97
PP5–PP1	0.897	0.114	11.27
PP5–PP2	0.456	0.072	13.63
			av 13.5

[a] Percent contribution of the second term to the first term in the right-hand side of eq 4.

The β_s values are accurate to ± 2 TPa^{-1}. The deviation in adiabatic compressibility $\Delta\beta_s$ from the ideal value, assumed to be additive in terms of molar fraction, is estimated by using the relation

$$\Delta\beta_s = \beta_s - \{X_1\beta_{s,1} + (1 - X_1)\beta_{s,2}\} \tag{2}$$

where β_s, $\beta_{s,1}$, and $\beta_{s,2}$ are the adiabatic compressibilities of the mixtures and the pure components respectively. Similarly the excess ultrasonic velocity (Δc) is computed by using the relation

$$\Delta c = c - \{X_1 c_1 + (1 - X_1)c_2\} \tag{3}$$

The excess properties of equimolar mixtures obtained at 298.16 K are presented in Table III.

Discussion

The variation of both c and β_s values as a function of X_1 are not found to be linear in all the binary mixtures studied. The change in ultrasonic velocity with change in solute concentration X_1, i.e., dc/dX_1, is provided by the properties of solute–solvent interaction. It can be seen from Table II and Table III that in general the variation of adiabatic compressibility with concentration bears an opposite sign to that of variation of ultrasonic velocity with concentration. This fact can be explained by differentiating eq 1 logarithmically with respect to concentration, yielding

$$\frac{1}{c}\frac{dc}{dX_1} = -\frac{1}{2}\left[\frac{1}{\beta_s}\frac{d\beta_s}{dX_1} + \frac{1}{\rho}\frac{d\rho}{dX_1}\right] \tag{4}$$

In general, for the liquid mixtures studied the contribution of the second term on the right-hand side of the eq 4 is only about 13.5% of the first term, as can be seen from Table IV. Therefore, change in velocity with concentration bears an opposite sign to that of the change in adiabatic compressibility with concentration. The above argument is valid in all the binary mixtures studied except for the PP5–PP1 binary mixture.

It has been observed with the excess compressibility becomes increasingly negative as the strength of interaction between unlike molecules increases. The difference in the boiling points of the two components is taken (*5*) as a rough measure of the strength of interaction. Figure 1 presents the $\Delta\beta_s$ versus difference in boiling points for six fluorocarbon binary liquid mixtures. It can be seen that the excess compressibility $\Delta\beta_s$ at equimolar mixture of the systems studied, in general, shows

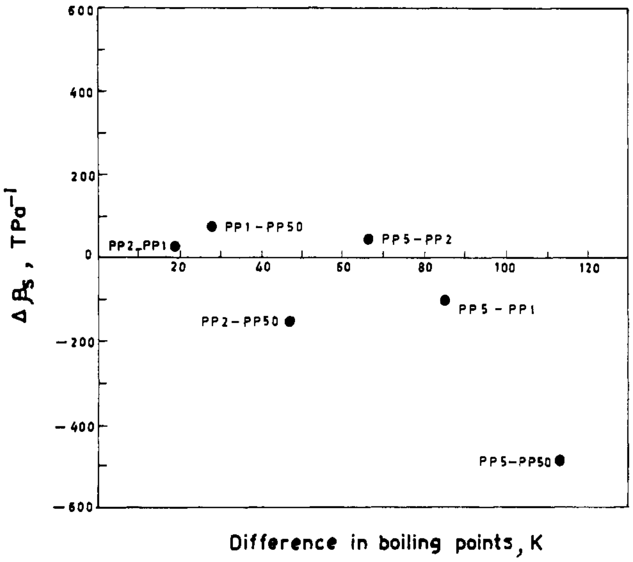

Figure 1. Plot of $\Delta\beta_s$ at equimolar mixture as a function of difference in bp's in six fluorocarbon binary mixtures.

a decreasing trend with increase in difference of boiling points.

This study leads to the possibility of obtaining any desired ultrasonic velocity in the range 477–714 ms^{-1} at 298.16 K, by mixing two distinct fluorocarbon liquids in a definite proportion. The same desired velocity can be obtained by various permutations of fluorocarbon binary liquid mixtures. One can have the choice of selecting an appropriate binary mixture depending on its characteristic impedance suited to the required application.

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Registry No. Flutec PP50, 678-26-2; Flutec PP1, 355-42-0; Flutec PP5, 306-94-5; Flutec PP2, 355-02-2.

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Vapor–Liquid Equilibria for the Chlorobenzene–Nitrobenzene System at 80.0 and 95.0 °C

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Isothermal vapor–liquid equilibrium (VLE) data for the binary system chlorobenzene–nitrobenzene were measured at temperatures of 95.0 and 80.0 °C and total system pressures between 10 and 260 mmHg using a dynamic still. The data obtained in this study are thermodynamically consistent according to the point-to-point consistency test. From these data, the UNIFAC parameters were estimated for the aromatic chloro (ACCl)/aromatic nitro (ACNO2) functional group interactions. These data were also correlated with four liquid-phase activity coefficient models (UNIQUAC, NRTL, Wilson, Van Laar), with the parameters estimated from the maximum-likelihood method.

Introduction

The UNIFAC method is widely used in process engineering applications, especially in phase-equilibrium calculations. This method is very useful in predicting the vapor–liquid equilibrium (VLE) of a system in the absence of experimental information. The UNIFAC method is used to predict activity coefficients in a liquid phase consisting of nonelectrolytic, nonpolymeric mixtures and within a temperature range of 300–425 K and pressures up to a few atmospheres. Fredenslund et al. (*1*) originally developed the UNIFAC method; it was later revised and its applicability range extended by Skjold-Jorgensen et al. (*2*) and Gmehling et al. (*3*).

The main aim of this study was to extend the UNIFAC group interaction parameter table (*3*) by determining the binary interaction parameters between the aromatic chloro/aromatic nitro (ACCl/ACNO2) groups. The parameter estimation technique used is described in Fredenslund et al. (*1*). Isothermal VLE data were measured for the chlorobenzene–nitrobenzene system at 80.0 and 95.0 °C. Only a few data sets for mixtures with aromatic nitro groups have been reported. Nitrobenzene is an industrially important chemical, mainly used in the manufacture of aniline and nitro–chloro derivatives, such as from the nitration of chlorobenzene (*4*).

Equipment and Experiments

The compounds used in this study were chlorobenzene and nitrobenzene. All chemicals were available in relatively high stated purity of at least 99+%. Each chemical was then analyzed on a gas chromatograph to assure the purity of the samples. Extra precautions were taken in handling chlorobenzene and nitrobenzene. A fume hood was used to store these chemicals. Protective equipment such as respirators, clothing, gloves, and eye protection was used according to the standards described in the Material Safety Data Sheets (MSDS) for chlorobenzene and nitrobenzene.

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