Sound Velocities and Related Properties in Ternary Solutions of *o*-Xylene

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Ultrasonic velocity, adiabatic compressibility, intermolecular free length, and free volume at 23 °C have been reported here for ternary liquid mixtures of I, *o*-xylene–acetone–benzene; II, *o*-xylene–acetone–cyclohexane; and III, *o*-xylene–acetone–carbon tetrachloride. For systems I and II the excess values are always negative, for III excess compressibility and free length are negative but excess free volume is both positive and negative.

Ultrasonic study of thermodynamic properties for binary liquid mixtures has been made by several workers (*6, 9, 14*). Few ternary mixtures have also been attempted (*11, 12*). The nonrectilinear behavior of velocities and adiabatic compressibilities of liquid mixtures with changing mole fractions are attributed to the difference in size of the molecules and the strength of the interaction. Fort and Moore (*5*) have compared the sign of excess compressibility with that of excess volume. Kaulgud (*8*) and Bhimasenachar et al. (*13*) have used the excess free length of binary mixtures to demonstrate the strength of the interaction between the components. Deshpande and Bhatgadde (*2*) have compared the excess free volume of binary systems with the strength of the interaction between the molecules. The ternary mixtures have not been attempted in detail. This paper deals with the results obtained from the study of ternary mixtures I (*o*-xylene–acetone–benzene), II (*o*-xylene–acetone–cyclohexane), and III (*o*-xylene–acetone–carbon tetrachloride) with regard to ultrasonic velocity, adiabatic compressibility, intermolecular free length, free volume, and their excess values.

Experimental Section

Materials. All chemicals used were of E. Merck grade and were redistilled and further purified by standard methods described by Weissberger (*15*). The calculated volumes of the liquids were added to one another to get mixtures of different known compositions. The mixtures were kept for 2 h and then they were used for velocity measurements.

Sound Velocity Measurements. The ultrasonic velocities were measured at 5 MHz, by using the Debye–Sears (*1*) light diffraction method. The source of ultrasonic wave was a generator comprising of an oscillator unit and a gold-plated circular quartz crystal of 2.54 cm diameter as transducer. A suitably designed (*10*) optical cell was used for keeping the solution and, with the help of a filter, light of wavelength 3657 Å from a mercury vapor lamp was allowed to fall normally to the path of ultrasonic waves. Such waves traversing in a liquid set up a periodical inhomogeneity which acts as an optical grating. The diffraction patterns were photographed on orthochromatic Agfa plates and the fringe widths were measured by a comparator reading correctly to the fourth decimal place. The maximum uncertainty in the velocity measurement was ±0.18%.

Density Measurements. The densities of liquids and mixtures were determined by a double-walled pycnometer having capillaries of narrow bore provided with well-fitting glass caps in order to avoid changes in composition because of evaporation of more volatile component. The pycnometer was calibrated with distilled water and benzene, and buoyancy corrections were made. The densities were reproducible to 1 part in 10^4.

Calculations. According to Eyring et al. (*4*) free volume, V_f, can be calculated from the velocity of sound in liquid medium C_l and that in the vapor C_g, by the relation below, V being the molar volume.

$$V_f = V\left(\frac{C_g}{C_l}\right)^3 \tag{1}$$

This equation has been used to calculate the free volume in the above ternary mixtures. The value of C_g for each component in the mixtures was obtained from the relation

$$C_g = \frac{C_p}{C_v}\frac{RT}{M}\left[1 + \frac{9}{128}\frac{P}{P_C}\frac{T_c}{T}\left(1 - 6\frac{T_c^2}{T^2}\right)\right]^{1/2} \tag{2}$$

where M is the molecular weight, P is the pressure, T_C and P_C are the critical temperature and pressure, respectively, C_p and C_v are the two specific heats, and R is the gas constant. C_p and C_v in the vapor phase were obtained by the method of Dobratz (*3*). For the calculation of V_f according to eq 1, the additivity of C_g has been assumed in the case of mixtures.

Jacobson's formula (*7*) has been used to calculate the intermolecular free length L_f from the following expression

$$L_f = K(\beta_s)^{1/2} \tag{3}$$

where β_s is the adiabatic compressibility, obtainable from the equation $\beta_s = (C_l^2\rho)^{-1}$, ρ being the density. K is a temperature-dependent constant whose values are given by Jacobson. Zero frequency results have been derived from high frequency data for use in deriving the thermodynamic properties.

The excess values, A^E, have been obtained from the expression

$$A^E = (A)_{mix} - (X_1A_1 + X_2A_2 + X_3A_3) \tag{4}$$

where A represents the parameters such as compressibility, free length, and free volume, and X_1, X_2, and X_3 are the mole fractions of the components whose parameters are A_1, A_2, and A_3, respectively.

Results

In Table II, X_1 is the mole fraction of acetone and X_2 is the mole fraction of benzene, cyclohexane, and carbon tetrachloride, respectively. Mole fraction of *o*-xylene was kept fixed at 0.4.

Discussion

Results of Table II show that for systems I and II the excess adiabatic compressibility and excess free volume have same sign throughout. In case III, β_s^E is negative at all compositions while V_f^E is negative at some compositions and positive at others. The deviation in compressibility from ideality is considerable, maximum being −4.46 for I, −4.22 for II and III. The magnitude of excess free volume and excess free length is very small. The negative deviation is indicative of strong interaction between the components of the mixture. However, the systems being ternary it is not possible, at this stage, to predict the mode of interaction. The work is still in progress.

Table I. Ultrasound Velocity and Related Properties in Pure Liquids at 23 °C

Liquid	C_l, m s^{-1}	C_g, m s^{-1}	$10^{12}\beta_s$, cm^2 dyn^{-1}	L_f, Å	V_f, ml	C_p	C_v
o-Xylene	1367	153.05	61.94	0.4896	0.1720	29.34	26.09
Acetone	1200	216.53	88.33	0.5846	0.4336	18.76	16.23
Benzene	1310	185.15	66.73	0.5082	0.2523	20.26	17.55
Cyclohexane	1257	174.48	81.87	0.5628	0.2912	27.49	24.69
Carbon tetrachloride	928	132.84	73.30	0.5326	0.2841	19.89	17.58

Table II. Ultrasound Velocity and Related Properties in Ternary Liquid Mixtures at 23 °C

X_1	X_2	C_l, m s^{-1}	C_g, m s^{-1}	$10^{12}\beta_s$, cm^2 dyn^{-1}	β_s^E	L_f, Å	L_f^E	V_f, ml	V_f^E
				I. *o*-Xylene–Acetone–Benzene					
0.00	0.60	1342	172.24	64.22	−0.59	0.4984	−0.0014	0.2179	−0.0023
0.10	0.50	1335	175.45	65.24	−1.73	0.5024	−0.0060	0.2304	−0.0079
0.20	0.40	1329	178.59	66.33	−2.80	0.5065	−0.0095	0.2422	−0.0142
0.30	0.30	1320	181.73	67.66	−3.63	0.5116	−0.0121	0.2561	−0.0185
0.40	0.20	1307	184.86	69.44	−4.01	0.5183	−0.0130	0.2727	−0.0200
0.50	0.10	1296	188.00	71.15	−4.46	0.5247	−0.0143	0.2890	−0.0218
0.60	0.00	1281	191.14	73.55	−4.22	0.5334	−0.0132	0.3098	−0.0192
0.50	0.50	1279	200.84	74.92	−2.61	0.5384	−0.0080	0.3157	−0.0273
				II. *o*-Xylene–Acetone–Cyclohexane					
0.00	0.60	1311	165.91	72.04	−1.86	0.5279	−0.0056	0.2334	−0.0101
0.10	0.50	1305	170.11	72.69	−1.85	0.5303	−0.0054	0.2472	−0.0106
0.20	0.40	1300	174.32	73.02	−2.17	0.5315	−0.0064	0.2603	−0.0117
0.30	0.30	1295	178.52	73.30	−2.54	0.5325	−0.0076	0.2740	−0.0122
0.40	0.20	1291	182.73	73.45	−3.03	0.5331	−0.0091	0.2861	−0.0144
0.50	0.10	1286	186.93	73.53	−3.60	0.5334	−0.0110	0.2983	−0.0164
0.60	0.00	1281	191.14	73.55	−4.22	0.5334	−0.0132	0.3098	−0.0192
0.50	0.50	1227	191.51	86.68	+1.58	0.5792	+0.0055	0.3744	−0.0120
				III. *o*-Xylene–Acetone–Carbon Tetrachloride					
0.00	0.60	1091	140.92	67.11	−1.65	0.5095	−0.0059	0.2315	−0.0078
0.10	0.50	1115	149.29	67.59	−2.67	0.5114	−0.0092	0.2521	−0.0021
0.20	0.40	1141	157.66	68.19	−3.57	0.5137	−0.0121	0.2705	+0.0013
0.30	0.30	1169	166.03	69.24	−4.03	0.5176	−0.0134	0.2872	+0.0031
0.40	0.20	1197	174.40	70.68	−4.09	0.5230	−0.0132	0.3020	+0.0029
0.50	0.10	1235	182.77	72.07	−4.20	0.5281	−0.0133	0.3090	−0.0050
0.60	0.00	1281	191.14	73.55	−4.22	0.5334	−0.0132	0.3098	−0.0192
0.50	0.50	1014	174.69	78.30	−2.52	0.5504	−0.0082	0.4354	+0.0765

Glossary

- C ultrasound velocity, m s^{-1}
- L_f free length, Å
- V_f free volume, ml
- β_s adiabatic compressibility, cm^2 dyn^{-1}
- P pressure
- R gas constant (8.314 × 10^7 ergs)
- T absolute temperature
- M molecular weight

Subscript

- C critical constants
- g gas phase
- l liquid phase

Superscript

- E excess function

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