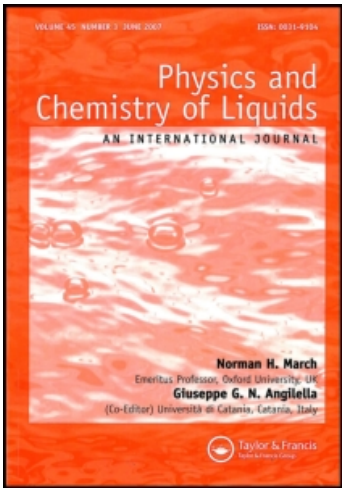

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Speed of Sound and Isentropic Compressibilities of *N*-Methylcyclohexylamine with Benzene and Substituted Benzenes at 303.15 K

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SPEED OF SOUND AND ISENTROPIC COMPRESSIBILITIES OF *N*-METHYLCYCLOHEXYLAMINE WITH BENZENE AND SUBSTITUTED BENZENES AT 303.15 K

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New experimental sound velocity and density data for binary mixtures of *N*-methylcyclohexylamine with benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, chlorobenzene, bromobenzene and nitrobenzene at 303.15 K have been reported. The sound velocity data were also used to compute the isentropic compressibilities (K_s). The deviation in isentropic compressibilities (ΔK_s) from ideal behaviour suggests that the existence of weak dipole-induced dipole and dipole–dipole interactions between unlike molecules.

Keywords: Sound speed; compressibility; polarizability

INTRODUCTION

Several workers [1–3] have made use of speed of sound and density data, evaluated from measured excess volume data to compute, isentropic compressibility. A survey of the literature showed that isentropic compressibility data for cyclohexylamine with alcohols [4], alkanes [5] and benzene and substituted benzenes [6] have been

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measured at 303.15 K. Further, the data for sound speed and isentropic compressibilities have been measured for mixtures of *N*-methylcyclohexylamine with 1-alcohols [7] at 303.15 K. However, no attempt has been made to measure isentropic compressibilities of binary mixtures of *N*-methylcyclohexylamine with benzene and substituted benzenes. Hence we report here new experimental sound velocity data for eight binary mixtures of *N*-methylcyclohexylamine with benzene and substituted benzenes.

EXPERIMENTAL METHOD

All the chemicals used were of analytical grade. They were further purified by the methods described else where [8] and were fractionally distilled through a fractionating column having thirty theoretical plates. The purity of the samples was checked by comparing the measured densities with those reported in literature [8, 9]. The densities of all compounds were measured by a bicapillary pycnometer with an accuracy of 2 parts per 10^5. The measured densities were presented along with those of literature values in Table I.

Ultrasonic velocities were measured by a single crystal ultrasonic interferometer with a frequency of 3 Hz at 303.15 K and the measured values were accurate to 0.02 percent. The temperature was maintained by circulating water around liquid cell from a thermostat controlled at a temperature of 303.15 K ± 0.01 K. The densities of the liquid mixtures at each composition have been computed from molar excess

TABLE I Densities of pure compounds at 303.15 K

	Density	*ρ(gm/cc)*
Compounds	*Experiment*	*Literature* [8, 9]
N-methylcyclohexylamine	0.84687	0.84690
Benzene	0.86846	0.86850
Toluene	0.85764	0.85770
o-xylene	0.87155	0.87160
m-xylene	0.85549	0.85551
p-xylene	0.85225	0.85230
Chlorobenzene	1.09553	1.09550
Bromobenzene	1.48154	1.48150
Nitrobenzene	1.19346	1.19341

volumes (V^E), reported earlier [10], using the relation

$$\rho = \frac{x_1 m_1 + x_2 m_2}{V_0 + V^E} \tag{1}$$

where x and m are the molefraction and molecular weight of the component respectively. V_0 and V^E stand for the ideal molar volume and excess molar volume respectively of ideal mixture. Isentropic compressibility (K_s) data have been computed using the relation

$$K_s = U^{-2}\rho^{-1} \tag{2}$$

where U and ρ denote sound velocity and density respectively. Further, the deviation in isentropic compressibility (ΔK_s) obtained using the equation.

$$\Delta K_s = K_s - \phi_1 K_{s1} - \phi_2 K_{s2} \tag{3}$$

where K_s, K_{s1} and K_{s2} are the isentropic compressibilities of the mixture and the pure components 1 and 2, ϕ_1 and ϕ_2 are the volume fractions of components 1 and 2, respectively.

RESULTS AND DISCUSSION

The experimental values for densities, ρ sound velocities U, isentropic compressibilities, K_s and ΔK_s, deviation in isentropic compressibility for all the eight binary systems are listed in Table II. Further, the experimental ΔK_s values against volume fraction are also graphically presented along with those for mixtures of benzene, toluene, *o*-xylene, *m*-xylene and *p*-xylene with *N*-methylcyclohexylamine in Figure 1 and ΔK_s data for the mixtures of chlorobenzene, bromobenzene and nitrobenzene with *N*-methylcyclohexylamine in Figure 2. The dependence of ΔK_s on volume fraction has been expressed by the polynomial of the form

$$\Delta K_s = \phi_1\phi_2[b_0 + b_1(\phi_1 - \phi_2) + b_2(\phi_1 - \phi_2)^2] \tag{4}$$

where b_0, b_1 and b_2 are constants. The values of these parameters can be evaluated by the method of least-squares and are given in Table III, along with standard deviation $\sigma(\Delta K_s)$ values.

TABLE II Volume fractions ϕ_1 of *N*-methylcyclohexylamine, density ρ, sound velocity U, isentropic compressibility K_s (from Eq. (2)) and deviation in isentropic compressibility ΔK_s (from Eq. (3))

ϕ_1	ρ (g/cm^3)	U m/sec	K_s TPa^{-1}	ΔK_s TPa^{-1}
		N-methylcyclohexylamine + benzene		
0.0000	0.86846	1276	707	–
0.1525	0.86605	1306	677	−21
0.2389	0.86412	1308	676	−16
0.4035	0.85965	1297	692	10
0.5035	0.85667	1290	702	26
0.6465	0.85282	1288	704	37
0.7526	0.85034	1302	694	34
0.8248	0.84900	1314	682	26
0.9665	0.84718	1344	653	6
1.0000	0.84687	1353	645	0
		N-methylcyclohexylamine + toluene		
0.0000	0.85764	1282	709	0
0.1992	0.85575	1287	704	8
0.2995	0.85453	1293	700	11
0.4875	0.85917	1301	693	16
0.5582	0.85100	1303	692	19
0.5933	0.85052	1311	684	19
0.7309	0.84876	1319	677	15
0.7822	0.84821	1330	666	12
0.9038	0.84715	1346	652	6
1.0000	0.84687	1353	642	0
		N-methylcyclohexylamine + *o*-xylene		
0.0000	0.87155	1329	50	0
0.1367	0.86767	1330	649	2
0.2008	0.86600	1333	649	2
0.3028	0.86313	1336	649	1
0.4823	0.85810	1340	649	2
0.5713	0.85570	1343	648	1
0.6988	0.85248	1345	647	1
0.7929	0.85037	1348	647	1
0.9329	0.84778	1351	646	1
1.0000	0.84687	1353	645	0
		N-methylcyclohexylamine + *m*-xylene		
0.0000	0.85549	1303	688	0
0.2071	0.85339	1311	682	4
0.4102	0.85139	1316	678	6
0.4828	0.85073	1321	674	6
0.5565	0.85002	1325	670	5
0.6084	0.84926	1328	667	4
0.6494	0.84922	1331	665	4
0.7905	0.84811	1335	662	4
0.8972	0.84742	1345	652	3
1.0000	0.84687	1353	645	0

TABLE II (Continued)

ϕ_1	ρ (g/cm^3)	U m/sec	K_s TPa^{-1}	ΔK_s TPa^{-1}
		N-methylcyclohexylamine + *p*-xylene		
0.0000	0.85225	1292	703	0
0.2055	0.85205	1300	694	−6
0.2643	0.85175	1310	684	−7
0.3645	0.85105	1318	675	−5
0.4017	0.85071	1323	672	−5
0.6304	0.84863	1329	667	−4
0.6425	0.84849	1334	662	−3
0.8125	0.84726	1342	655	0
0.8588	0.84704	1348	650	3
1.0000	0.84687	1353	645	0
		N-methylcyclohexylamine + chlorobenzene		
0.0000	1.09553	1249	585	0
0.2245	1.03976	1261	605	4
0.2602	1.03114	1268	603	5
0.5233	0.96570	1283	629	12
0.6234	0.93988	1298	632	10
0.6631	0.93084	1305	630	6
0.8208	0.89161	1331	634	2
0.0000	0.84687	1353	645	0
		N-methylcyclohexylamine + bromobenzene		
0.0000	1.48154	1138	500	0
0.0964	1.42033	1157	526	−10
0.1501	1.38625	1174	523	−16
0.2501	1.32273	1198	528	−24
0.3886	1.23471	1278	538	−31
0.4815	1.17388	1251	544	−37
0.5958	1.10142	1276	558	−33
0.7879	0.98043	1303	601	−20
0.9134	0.90181	1328	629	−9
1.0000	0.84687	1353	645	0
		N-methylcyclohexylamine + nitrobenzene		
0.0000	1.19346	1437	406	0
0.1857	1.12847	1426	436	−14
0.3081	1.08544	1415	460	−19
0.4053	1.05173	1408	480	−23
0.5021	1.01802	1402	500	−25
0.5876	0.98736	1396	520	−26
0.7031	0.94896	1386	549	−25
0.7840	0.92121	1375	574	−19
0.9139	0.87610	1363	614	−10
1.0000	0.84687	1353	645	0

The experimental ΔK_s values may be ascribed to the relative strengths of opposing effects which influence the free space defined by Jacobson [11]. Break up of amine aggregates by the addition of

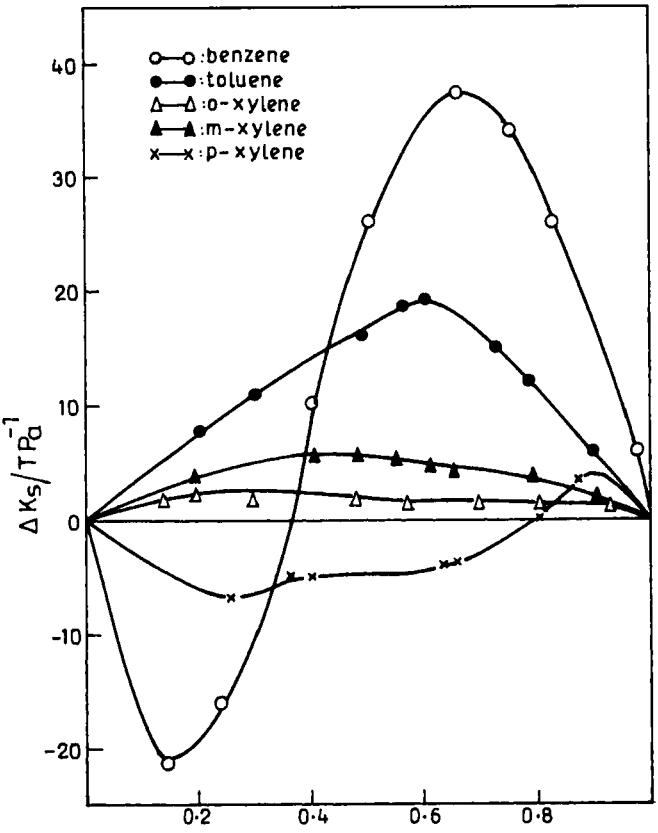

FIGURE 1 Volume fraction of *N*-methylcyclohexylamine.

benzene or substituted benzene and loss of dipolar association of both the amine and benzene leads to increase in free spaces in mixtures contributing to negative deviations in sound velocity and positive deviation in compressibility. However, this effect will be counteracted by the complex formation between unlike molecules through N—H.....π interaction would reduce in free spaces in mixtures leading to negative deviation in compressibility. The actual values of ΔK_s, therefore, would depend upon relative strengths of the above said opposing effects.

An examination of curves in Figures 1 and 2 show that ΔK_s values are negative over entire range of composition for the systems

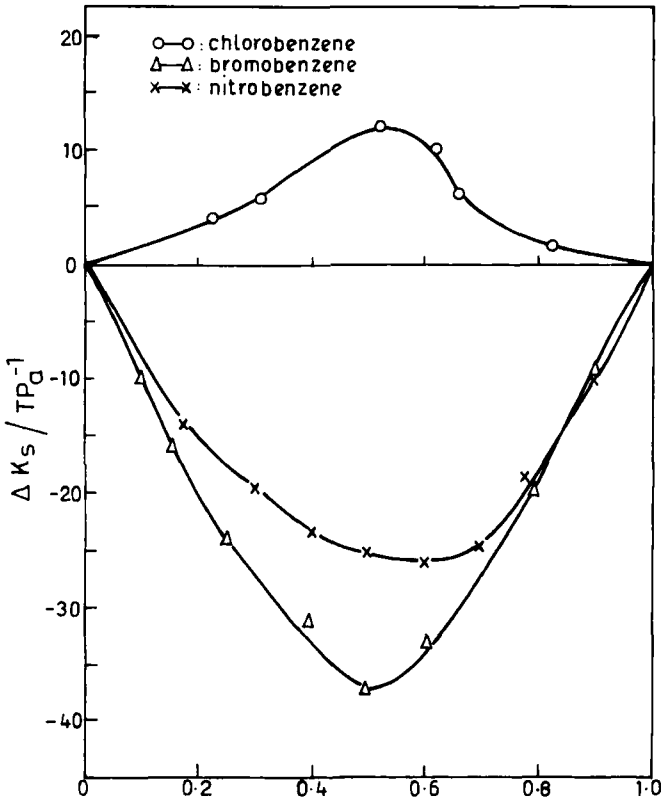

FIGURE 2 Volume fraction of *N*-methylcyclohexylamine.

N-methylcyclohexylamine with *p*-xylene, bromobenzene, and nitrobenzene. On the other hand, the quantity is positive for mixtures of *N*-methylcyclohexylamine with toluene, *o*-xylene, *m*-xylene and chlorobenzene.

Further, in the binary system *N*-methylcyclohexylamine with benzene the K_s values exhibits an inversion in sign at lower volume fraction of *N*-methyl cyclohexylamine. Hence, in this case the above said factors, which are responsible for deviation in compressibility cancel each other.

The algebraic ΔK_s values fall in the order: benzene > *p*-xylene > *m*-xylene > toluene > *o*-xylene > chlorobenzene > bromobenzene > nitrobenzene. The above order suggests that the extent of interactions

TABLE III Values of the parameters b_0, b_1 and b_2 of the Eq. (4) and the standard deviation of $\sigma(\Delta K_s)$ at 303.15 K

System	b_0	b_1	b_2	$\sigma(\Delta K_s)$
		TPa^{-1}		TPa^{-1}
N-methylcyclohexylamine + benzene	99.998	267.988	−188.395	1
N-methylcyclohexylamine + toluene	70.774	22.217	−30.028	1
N-methylcyclohexylamine + *o*-xylene	3.937	−3.25	18.293	1
N-methylcyclohexylamine + *m*-xylene	19.946	−1.252	17.683	1
N-methylcyclohexylamine + *p*-xylene	−21.801	33.601	24.003	2
N-methylcyclohexylamine + chlorobenzene	42.303	13.501	−30.752	1
N-methylcyclohexylamine + bromobenzene	−138.662	2.213	37.464	1
N-methylcyclohexylamine + nitrobenzene	−101.072	−24.072	−0.050	1

between unlike molecules decreases with polarizability [8] value and proper dipole alignment of the components.

References

[1] Iloukhani, H., Dayananda Reddy, K. and Prabhakara Rao, M. V. (1985). *Acoustics Letters*, **8**, 143.
[2] Krishnaiah, A. and Naidu, P. R. (1980). *Acta Chim. Acad. Sci. Hung.*, **104**, 43.
[3] Reddy, K. S., Venkateswarlu, R. and Rajesekhar, P. (1989). *Indian J. Technol.*, **27**, 221.
[4] Dharmaraju, G., Venkateswarlu, P. and Raman, G. K. (1982). *Chemica Scripta*, **19**, 140.
[5] Dharmaraju, G., Narayanaswamy, G. and Raman, G. K. (1981). *Indian J. Chem.*, **20**, 1109.
[6] Dharmaraju, G., Narayanaswamy, G. and Raman, G. K. (1982). *Indian J. Pure and Applied Phys.*, **20**, 162.
[7] Chennarayappa, C., Rambabu, K., Venkateswarlu, P. and Raman, G. K. (1991). *Acoustics Letters*, **15**, 83.
[8] Riddick, J. A. and Bunger, W. B., *Organic Solvents* (Wiley Inter-Science, New York, 1970).
[9] Timmeramans, J., *Physico-Chemical constants of pure organic compounds* (Elsevier publishing Co., Amsterdam, 1950).
[10] Prabhavathi, C. L., Siva Kumar, K., Venkateswarlu, P. and Raman, G. K., *Indian J. Chem.* (Communicated).
[11] Jacobson, B. (1953). *Arkiv. Kemi.*, **2**, 177.