



Thermodynamic and Acoustic properties of binary liquid mixtures of octan-2-ol with benzene and halobenzenes at 308.15 K

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Abstract: Densities ρ , and speeds of sound u , of binary mixtures of octan-2-ol with benzene, chlorobenzene and bromobenzene have been measured over the entire range of composition at 308.15 K and atmospheric pressure. From the experimental V^E data, excess molar κ_s volumes, isentropic compressibilities, excess isentropic compressibilities κ_s^E , and deviations of speeds of sound u^D have been calculated at 308.15 K. These excess functions have been fitted to the Redlich-Kister polynomial equation.

Keywords: Octan-2-ol; Aromatic hydrocarbon; Aromatic halohydrocarbon; Excess molar volume.

I. Introduction

This paper is a continuation of our work related to the study of thermodynamic, acoustic and transport properties of binary mixtures of higher alcohols with aliphatic haloalkanes and aromatic halohydrocarbons. The measurements of these properties have been utilized in recent years in understanding the nature of molecular systems and physico-chemical behavior of binary and multi-component liquid mixtures [1-6]. In an attempt to explore the nature of interactions occurring between the mixing components, the densities, ρ , and speeds of sound, u , of binary mixtures of octan-2-ol with benzene (ben), chlorobenzene (Cl-ben) and bromobenzene (Br-ben) have been measured over the entire range of composition at 308.15 K and atmospheric pressure. The related quantities viz.; excess molar volumes V^E , isentropic compressibilities κ_s , excess isentropic compressibilities κ_s^E , and deviations of speeds of sound u^D have been calculated over the whole composition range at 308.15 K and atmospheric pressure. All the excess functions have been fitted to the Redlich-Kister polynomial equation to derive the polynomial coefficients, A_i , and the standard deviation, σ , between the experimental and the calculated quantities.

II. Experimental Section

The mole fraction purity of the liquids from s. d. fine Chemical Ltd. was as follows: benzene (99.7 %), chlorobenzene (99.7 %), bromobenzene (99.0 %) and from Merck chemicals ltd. was as follows octan-2-ol (99.9 %). The mass fraction of water for liquids under test was as follow: benzene (0.05 %), chlorobenzene (0.03 %), bromobenzene (0.05 %) and octan-2-ol (0.03 %). Prior to experimental measurements, all liquids were stored in dark bottles over 0.4 nm molecular sieves to reduce water content and were partially degassed with a vacuum pump under nitrogen atmosphere. Densities and speeds of sound of the pure liquids and their mixtures were measured with density and sound speed analyzer (Anton Paar DSA 5000). Both the speeds of sound and densities are extremely sensitive to temperature, so the temperature was kept constant within ± 0.001 K using the peltier method. Before each series of measurements, the calibration of the apparatus was carried out with double distilled, deionised water ($\rho=997.047$ kg m⁻³), benzene and toluene at the desired temperatures. The densities have precision better than ± 0.0020 kg m⁻³ and the speeds of sound values have precision better than ± 0.01 m s⁻¹. The uncertainty of the density measurements was estimated to be ± 0.020 kg m⁻³ and uncertainty of the speeds of sound measurements was estimated to be ± 1 m s⁻¹.

The purities of all the samples were determined by comparing the measured densities, and speeds of sound of pure liquid components at 308.15 K with the literature [7-16] values given in Table 1.

III. Results and Discussion

The experimental results for densities ρ , volume fraction, ϕ speeds of sound u , isentropic compressibilities κ_s , excess molar volumes V^E , deviation in speeds of sound u^D , and excess isentropic compressibilities κ_s^E , for binary liquid mixtures at 308.15 K are reported in Table 2.

The excess molar volumes V^E , of the solutions were calculated from the densities of the pure liquids and their mixtures using the following equation:

$$V^E = (x_1 M_1 + x_2 M_2) / \rho - (x_1 M_1 / \rho_1 + x_2 M_2 / \rho_2) \quad (1)$$

where ρ is the density of the mixture and x_1 , M_1 , ρ_1 and x_2 , M_2 and ρ_2 are the mole fraction, molecular weight, and the density of pure components, respectively.

From the results of speeds of sound, the isentropic compressibility κ_s , was calculated as

$$\kappa_s = 1/u^2 \rho \quad (2)$$

The corresponding excess isentropic compressibilities κ_s^E , were obtained from the relations [3,6,7,17]

$$\kappa_s^E = \kappa_s - \kappa_s^{id} \quad (3)$$

where the isentropic compressibility term κ_s^{id} was computed using the relation [6,7,17]

$$\kappa_s^{id} = \sum_{i=1}^2 \phi_i \left[\kappa_{s,i} + \frac{TV_i(\alpha_i^2)}{C_{p,i}} \right] - \left\{ \frac{T \left(\sum_{i=1}^2 x_i V_i \right) \left(\sum_{i=1}^2 \phi_i \alpha_i \right)^2}{\sum_{i=1}^2 x_i C_{p,i}} \right\} \quad (4)$$

Here, $C_{p,i}$ is the molar heat capacity of the i^{th} component and α is the thermal expansion coefficient which has been calculated from the equation [6,7]

$$\alpha = (\partial V / \partial T)_p / V = -\rho^{-1} \cdot (\partial \rho^{-1} / \partial T)_p \quad (5)$$

The deviation of the speed of sound u^D , from the speed of sound of an ideal mixture is defined as [6,7]

$$u^D = u - u^{id} = u - (\rho^{id} \kappa_s^{id})^{-1/2} \quad (6)$$

$$u^{id} = (\rho^{id} \kappa_s^{id})^{-1/2} \quad (7)$$

where u is the speed of sound of the mixture, $\rho^{id} = \sum \Phi_i \rho_i$ is the density of corresponding ideal mixture [3] and ρ_i is the density of pure component i . The volume fraction, ϕ_i was calculated as

$$\Phi_i = \frac{x(i)v(i)^0}{v^{id}} \quad (8)$$

The results of V^E , u^D and κ_s^E have been fitted to the Redlich-Kister equation [18] of the type

$$\Delta Y = x_1(1-x_1) \sum_{k=1}^n A_k (1-2x_1)^{k-1} \quad (9)$$

where k is the number of estimated parameters and A_k , the polynomial coefficients were obtained by fitting the equation to the experimental results by least-squares regression method.

The standard deviations σ , for V^E , u^D and κ_s^E were calculated using the relation

$$\sigma(Y) = \left[\frac{\sum (y_{\text{expt}} - y_{\text{calc}})^2}{N - n} \right]^{1/2} \quad (10)$$

The coefficients of Redlich-Kister equation and standard deviations for excess molar volumes V^E , excess

isentropic compressibilities κ_s^E , and deviation in speeds of sound u^D , for binary liquid mixtures at 308.15 K are reported in Table 3.

The plots of V^E with mole fraction x_1 for the binary mixtures of octan-2-ol with benzene, chlorobenzene and bromobenzene at 308.15 K are depicted in Fig. 1. The V^E values are positive at this temperature for the systems over the whole composition range. The excess molar volume V^E , decreases in the sequence:

$V_{brben-oct}^E > V_{ben-oct}^E > V_{clben-oct}^E$. Since the molar volumes of octan-2-ol (161.027×10^{-6}) $\text{m}^3 \text{mol}^{-1}$, benzene (90.522×10^{-6}) $\text{m}^3 \text{mol}^{-1}$, chlorobenzene (112.559×10^{-6}) $\text{m}^3 \text{mol}^{-1}$ and bromobenzene (106.477×10^{-6}) $\text{m}^3 \text{mol}^{-1}$ at 308.15 K differ considerably, it appears that the aromatic hydrocarbon molecules intercalate between the polymeric entities of octan-2-ol and disrupt their H-bonding [3]. The excess molar volumes are influenced by (i) loss of dipolar association and differences in size and shape and (ii) dipole-dipole, dipole-induced dipole interactions, and charge transfer complexation between unlike molecules. The former effect leads to expansion in volume and the latter contributes to contraction in volume. The actual value of V^E depends on the balance between these two opposing contributions. The experimental data in the present study suggest that the factors which are responsible for expansion in volume are dominant in all the binary mixtures.

The curves for the deviations of speeds of sound u^D , vs x_1 , at 308.15 K are presented in Fig. 2 and their variations are of quite different nature than those of the molar excess volumes, V^E . The u^D values are negative

over the entire composition range for the benzene + octan-2-ol and the chlorobenzene + octan-2-ol systems but for the binary mixture bromobenzene + octan-2-ol, the curve is poorly sigmoidal. These values at the minimum of the curves vary in the following order: $u^D_{ben-oct} > u^D_{brben-oct} > u^D_{clben-oct}$.

The results of excess isentropic compressibilities κ^E_s , vs x_1 , at 308.15 K are presented in Fig. 3. The κ^E_s values are positive over the entire composition range for all the studied systems. The positive values at the maximum of these curves vary in the sequence: $\kappa^E_{s,ben-oct} > \kappa^E_{s,clben-oct} > \kappa^E_{s,brben-oct}$. The overall behavior of κ^E_s is similar to that of u^D (Fig. 2) for all the binary mixtures but is of opposite sign [19]. The positive values of κ^E_s imply higher compressibility of the binary liquid mixtures than the corresponding ideal mixtures. It can be pointed out that κ^E_s values decrease when the chlorine atom of the aromatic halohydrocarbon is substituted by a bromine atom [20].

IV. Conclusion

In this paper, the densities, and speeds of sound, of the binary mixtures of octan-2-ol with benzene, chlorobenzene, and bromobenzene have been experimentally determined at 308.15 K and the atmospheric pressure for the whole composition range and comparison with the data available in the literature has been made for the pure liquids and the binary mixtures. For the densities, and speeds of sound, good accordance has been found between the experimental and the literature values. The observed positive values of excess molar volume and excess isentropic compressibilities over the entire composition range for the studied mixtures confirm the weak physical intermolecular interactions between octan-2-ol and the aromatic-hydrocarbon molecules.

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Figure Captions

Fig. (1) Excess molar volumes V^E versus mole fraction x_1 at 308.15 K for binary mixtures of octan-2-ol with benzene ($\circ$), chlorobenzene ($\blacksquare$) and bromobenzene ($\blacktriangle$). The solid curves have been derived using Redlich-Kister equation

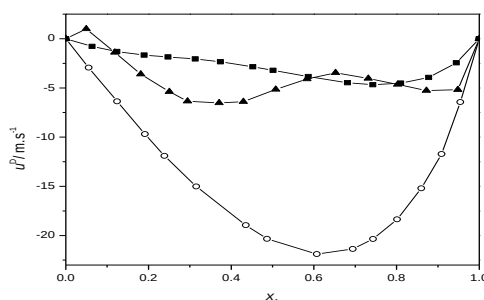


Fig. (2) Deviations of speeds of sound u^D versus mole fraction x_1 at 308.15 K for binary mixtures of octan-2-ol with benzene (○), chlorobenzene (■) and bromobenzene (▲). The solid curves have been derived using Redlich-Kister equation.

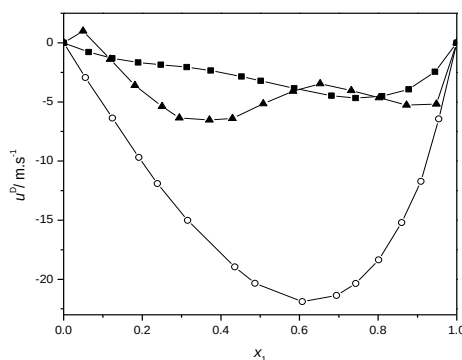


Fig. (3) Excess isentropic compressibilities K_S^E versus mole fraction x_1 at 308.15 K for binary mixtures of octan-2-ol with benzene (○), chlorobenzene (■) and bromobenzene (▲). The solid curves have been

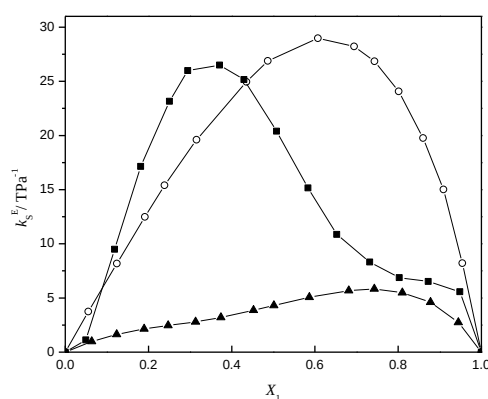


Table 1: Physical properties of pure liquid components at 308.15 K

Pure Liquid	$\rho / \text{kg m}^{-3}$		$u / \text{m s}^{-1}$	
	Expt	Lit	Expt	Lit
Octan-2-ol	0.816379	0.816444	1306.73	1305.22
Benzene	0.873659	0.873650	1299.04	1298.43
Chlorobenzene	1.090198	1.090178	1230.66	1231.34
Bromobenzene	1.474584	1.474412	1122.45	1123.40

Table 2: Densities ρ , speeds of sound u , excess molar volumes V^E , deviation in speeds of sound u^D , isentropic Compressibilities K_S , and Excess isentropic compressibilities K_S^E for benzene / halobenzenes (1) + octan-2-ol (2) at 308.15 K.

x_1	ϕ_1	ρ	u	$V^E \times 10^6$	u^D	K_S	K_S^E
		kg m^{-3}	m s^{-1}	$\text{m}^3 \text{mol}^{-1}$	m s^{-1}	TPa^{-1}	TPa^{-1}
Benzene (1) + 2-octanol (2)							
0.0000	0.0000	0.816379	1306.73	0.0000	0.00	717.36	0.00
0.0555	0.0319	0.817639	1302.11	0.1074	-2.94	721.35	3.75
0.1239	0.0734	0.819333	1296.61	0.2303	-6.37	725.97	8.18
0.1912	0.1170	0.821189	1291.26	0.3363	-9.69	730.35	12.49
0.2386	0.1494	0.822588	1287.64	0.4074	-11.90	733.21	15.41
0.3153	0.2052	0.825083	1282.29	0.5072	-15.01	737.11	19.61
0.4353	0.3017	0.829725	1275.09	0.6116	-18.95	741.28	24.95
0.4865	0.3468	0.831951	1272.45	0.6472	-20.34	742.37	26.88
0.6072	0.4642	0.838216	1268.54	0.6630	-21.88	741.37	28.97
0.6941	0.5598	0.843671	1268.11	0.6272	-21.36	737.08	28.23
0.7432	0.6186	0.847145	1269.01	0.5919	-20.35	733.01	26.85
0.8011	0.6930	0.851769	1271.43	0.5224	-18.35	726.26	24.07
0.8599	0.7748	0.857105	1275.79	0.4229	-15.21	716.82	19.76
0.9090	0.8485	0.862159	1281.11	0.3132	-11.72	706.71	15.01

0.9541	0.9210	0.867443	1288.93	0.1802	-6.44	693.91	8.21
1.0000	1.0000	0.873659	1299.04	0.0000	0.00	678.29	0.00
Chlorobenzene (1) + 2-octanol (2)							
0.0000	0.0000	0.808742	1270.84	0.0000	0.00	765.61	0.0000
0.0637	0.0418	0.820323	1265.82	0.0362	-0.93	760.80	0.2316
0.1236	0.0830	0.831735	1261.44	0.0658	-1.51	755.58	0.3768
0.1894	0.1303	0.844893	1256.81	0.0936	-2.01	749.31	0.4992
0.2474	0.1741	0.857040	1252.94	0.1197	-2.31	743.26	0.5786
0.3131	0.2261	0.871496	1248.62	0.1468	-2.68	735.99	0.6656
0.3740	0.2770	0.885597	1244.71	0.1737	-3.04	728.83	0.7473
0.4525	0.3464	0.904837	1239.86	0.2086	-3.54	718.93	0.8498
0.5014	0.3920	0.917496	1236.97	0.2287	-3.87	712.32	0.9103
0.5867	0.4764	0.940941	1232.25	0.2568	-4.50	699.91	1.0040
0.6813	0.5782	0.969326	1227.81	0.2713	-5.12	684.33	1.0587
0.7429	0.6495	0.989289	1225.74	0.2682	-5.24	672.79	1.0338
0.8098	0.7319	1.012572	1224.47	0.2439	-5.02	658.69	0.9330
0.8776	0.8214	1.038109	1224.52	0.1931	-4.31	642.43	0.7434
0.9446	0.9162	1.065556	1226.56	0.1069	-2.70	623.80	0.4247
1.0000	1.0000	1.090198	1230.66	0.0000	0.00	605.65	0.0000
Bromobenzene (1) + 2-octanol (2)							
0.0000	0.0000	0.808742	1270.84	0.0000	0.00	765.61	0.0000
0.0495	0.0333	0.822703	1261.16	1.5802	1.36	764.22	2.1447
0.1184	0.0816	0.846671	1246.49	2.9907	1.62	760.16	4.2044
0.1814	0.1278	0.871079	1233.91	3.9454	2.22	754.01	5.4737
0.2506	0.1811	0.900938	1220.88	4.6419	3.16	744.66	6.2554
0.2943	0.2162	0.922526	1212.92	4.7361	3.71	736.81	6.2336
0.3711	0.2806	0.963063	1199.96	4.7573	5.10	721.13	5.9093
0.4297	0.3325	0.997936	1191.64	4.4413	7.18	705.68	5.0270
0.5077	0.4054	1.048553	1182.56	3.8315	11.11	681.97	3.4682
0.5834	0.4808	1.102549	1174.23	3.0862	14.42	657.80	1.9361
0.6524	0.5538	1.155092	1166.63	2.4285	16.44	636.09	0.8071
0.7315	0.6430	1.221226	1156.58	1.5547	16.09	612.14	-0.1892
0.8025	0.7287	1.284269	1146.74	0.8843	13.55	592.13	-0.6140
0.8722	0.8186	1.349546	1136.44	0.3600	8.86	573.75	-0.6110
0.9483	0.9239	1.422795	1127.03	0.0860	3.43	553.33	-0.2742
1.0000	1.0000	1.474584	1122.45	0.0000	0.00	538.27	0.0000

Table 3: Coefficients of Redlich-Kister equation and standard deviations for all excess functions for benzene / halobenzenes (1) + octan-2-ol (2) at 308.15 K.

Property	A_1	A_2	A_3	A_4	σ
Benzene (1) + 2-octanol (2)					
$V^E \cdot 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$	2.6651	0.5651	0.6717	0.6994	0.0063
$u^D / (\text{m} \cdot \text{s}^{-1})$	-78.67	-43.07	-49.96	-31.33	0.14
$K_{S,m}^E / (\text{m}^3 \cdot \text{PPa}^{-1} \cdot \text{mol}^{-1})$	16.741	4.725	5.454	2.713	0.013
Chlorobenzene (1) + 2-octanol (2)					
$V^E \cdot 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$	0.9074	0.7717	0.5058	0.0342	0.00115
$u^D / (\text{m} \cdot \text{s}^{-1})$	-15.34	-14.04	-20.43	-6.03	0.09
$K_{S,m}^E / (\text{m}^3 \cdot \text{PPa}^{-1} \cdot \text{mol}^{-1})$	3.625	2.436	2.765	-0.267	0.0083
Bromobenzene (1) + 2-octanol (2)					
$V^E \cdot 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$	15.6964	-17.2878	0.7664	0.4585	0.0550
$u^D / (\text{m} \cdot \text{s}^{-1})$	44.25	90.87	12.94	-87.13	0.55
$K_{S,m}^E / (\text{m}^3 \cdot \text{PPa}^{-1} \cdot \text{mol}^{-1})$	14.619	-39.224	4.634	15.646	0.094