

Volumetric And Acoustic Properties Of Binary Liquid Mixtures Of Acetonitrile With 2-Ethoxyethanol And 2-Butoxyethanol At Different Temperatures

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Abstract: Ultrasonic velocity (u_m) and density (ρ_m) for binary mixtures of acetonitrile with 2-ethoxyethanol and acetonitrile with 2-butoxyethanol have been measured over the whole range of composition at temperatures 293K, 303K and 313K. Molar volumes and isentropic compressibility were calculated using experimental data. Excess molar volume (V_m^E), deviation in ultrasonic velocity (Δu), deviation in isentropic compressibility ($\Delta \kappa_s$) and excess molar isentropic compressibility (K_s^E) for binary mixtures of acetonitrile with 2-ethoxyethanol and 2-butoxyethanol respectively over the entire composition range at temperatures 293K, 303K and 313K were evaluated from ultrasonic velocity (u_m), density (ρ_m). Excess molar volume (V_m^E), deviation in ultrasonic velocity (Δu), deviation in isentropic compressibility ($\Delta \kappa_s$), excess molar isentropic compressibility (K_s^E) were fitted to the Redlich-Kister polynomial equation. The variations in thermodynamic parameters with composition and temperature have been discussed on the basis of dipole - dipole interactions and hydrogen bond complexes between unlike molecules. The observed positive and negative values of excess parameters were discussed in terms of strength of interactions in these binary systems.

Keywords: Ultrasonic velocity, Excess molar volume, deviation in ultrasonic velocity, deviation in isentropic compressibility.

I. INTRODUCTION

Measurements of physico-chemical properties such as density and ultrasonic velocity of pure components and their binary mixtures are being increasingly used as tools for investigations of the properties of pure components and the nature of intermolecular interactions between the components of liquid mixtures [1, 2]. Excess properties and deviation of properties for liquid mixture can reveal the existence of specific molecular interactions. Therefore, the systematic

study of these properties has great importance in gaining a better knowledge of these interactions [3, 4]. Moreover, the knowledge of the thermodynamic and transport properties is essential for the proper design of industrial processes.

Alkoxyethanols are widely used as industrial solvents. Studies involving the measurements of various thermodynamic properties of binary and ternary mixtures of alkoxyethanols with polar and nonpolar solvents are important for studying the effect of the simultaneous presence of etheric and hydroxyl groups of the molecular interaction. Such studies

also give important information about the unique nature of their self association in comparison with the associative behavior of simple alcohols. A literature survey shows that excess volumes and isentropic compressibilities of 2-butoxyethanols + n-alkanes, 2-butoxyethanols+ n-hexane+ n-heptane were studied by Benson [5] and Sastry [6] respectively.

Ultrasonic velocity (u_m) and density (ρ_m) for binary mixtures of Acetonitrile with 2-ethoxyethanol and 2-butoxyethanol respectively have been measured and reported. Molar volume and isentropic compressibility were calculated using experimental data. Excess molar volume (V_m^E), deviation in ultrasonic velocity (Δu), deviation in isentropic compressibility (Δk_s) for binary mixtures of acetonitrile with 2-ethoxyethanol and 2-butoxyethanol respectively over the entire composition range at temperatures 293K, 303K and 313K were evaluated from ultrasonic velocity (u_m) and density (ρ_m) data. Excess molar volume (V_m^E), deviation in ultrasonic velocity (Δu), deviation in isentropic compressibility (Δk_s) were fitted to the Redlich-Kister polynomial equation.

II. EXPERIMENTS DETAILS

The chemicals used were obtained from Ranbaxy, B.D.H., England, and E. Merck (India) Ltd., Mumbai.

A. DENSITY MEASUREMENT

Single-limbed calibrated pycnometer was used for determining the densities of the mixtures. The pycnometer stem, with uniform fine bore, had uniform graduations of 0.01 ml over it. To minimise the loss of liquid due to evaporation, Teflon cap was used for closing the open end of the capillary stem, with a small orifice to ensure that the pressure inside the capillary was equal to the atmospheric pressure. The weight of empty, wellcleaned and dried pycnometer was taken accurately by electronic balance (AR 2140, OHAUS, Parsippany, NJ, USA), and then the liquid was introduced into the bulb of the pycnometer with the help of hypodermic syringe having a needle long enough to reach the bottom of the bulb so as to avoid the undesired sticking of the solution to the inner wall of the pycnometer stem. Filled pycnometer was again weighed accurately. Possible error in the estimation of mole fraction is ± 0.0001 .

B. VELOCITY MEASUREMENT

The interferometric technique has been used for the determination of ultrasonic velocity. The apparatus is a variable path fixed frequency interferometer (Model F-81, Mittal Enterprises, New Delhi, India). It consists of a high frequency generator (2 MHz) and a double-walled measuring

cell. The accuracy in the measurement of speed of sound is found to be 0.1 m/s.

C. TEMPERATURE MAINTENANCE

Circulating water bath with programmable temperature controller (TC-502, Brookfield Engineering Laboratories, Inc., USA), having variable pump speeds, has been used for water circulation in water jackets of the apparatuses. The temperature controller covers the temperature measurement range of -20°C to 200°C with temperature stability of $\pm 0.01^\circ\text{C}$.

III. RESULT AND DISCUSSION

The experimental values of density (ρ_m) and ultrasonic velocity (u_m) for acetonitrile + 2-ethoxyethanol and acetonitrile+2-butoxyethanol mixtures at temperatures 293K, 303K and 313K are given in table 1. The values of V_m^E , Δu and Δk_s were plotted against the mole fraction of acetonitrile and are shown in figs. 1 to 3 respectively. The values of excess molar volume (V_m^E) for acetonitrile + 2-ethoxyethanol and acetonitrile + 2-butoxyethanol have been found to be negative over the entire composition range at all the temperature studied here. The negative V_m^E values are greater in acetonitrile + 2-ethoxyethanol system as compared to acetonitrile +2-butoxyethanol (fig.1).

x_1	ρ_m (g. cm ⁻³)			u_m (m.s ⁻¹)		
	293K	303K	313K	293K	303K	313K
acetonitrile+ 2-ethoxyethanol						
0.0000	0.9296	0.9207	0.9113	1328	1286	1244
0.1961	0.9176	0.9092	0.9014	1323	1283	1242
0.3544	0.9039	0.8952	0.8860	1319	1280	1240
0.4848	0.8879	0.8788	0.8701	1315	1277	1238
0.5941	0.8718	0.8626	0.8542	1312	1275	1237
0.6871	0.8560	0.8473	0.8381	1309	1272	1235
0.7671	0.8407	0.8318	0.8226	1306	1269	1233
0.8367	0.8261	0.8172	0.8082	1303	1267	1231
0.8978	0.8116	0.8024	0.7934	1300	1264	1229
0.9518	0.7983	0.7886	0.7796	1298	1262	1226
1.0000	0.7856	0.7752	0.7650	1296	1260	1224
acetonitrile+ 2-butoxyethanol						
0.0000	0.9016	0.8926	0.8841	1322	1291	1268
0.2423	0.8903	0.8817	0.8733	1317	1284	1259
0.4185	0.8784	0.8697	0.8610	1312	1279	1252
0.5523	0.8662	0.8570	0.8481	1309	1275	1247
0.6573	0.8534	0.8444	0.8356	1306	1272	1242
0.7422	0.8414	0.8324	0.8232	1304	1269	1238
0.8120	0.8295	0.8203	0.8114	1302	1267	1234
0.8704	0.8179	0.8086	0.7991	1300	1265	1231
0.9200	0.8068	0.7972	0.7879	1298	1263	1228
0.9628	0.7961	0.7862	0.7764	1297	1262	1226
1.0000	0.7856	0.7752	0.7650	1296	1260	1224

Table 1: The experimental values of density (ρ_m) and ultrasonic velocity (u_m) for both the mixtures at temperatures 293, 303 and 313K

According to Fort and Moore [7], a negative excess molar volume (V_m^E) is an indication of strong hetero-molecular interaction in the liquid mixtures and is attributed to charge-transfer, dipole-dipole interaction and hydrogen bonding between the unlike molecules, while a positive sign indicates a weak interaction and is attributed to dispersive forces. The magnitudes of the contribution will vary with the components and composition of the mixtures. In the present investigation, both the mixtures exhibited negative magnitude of excess molar volume (V_m^E). This depicts the presence of hetero-molecular interaction, which supports the view proposed by Fort and Moore. The negative values of V_m^E indicate that volume contraction takes place upon mixing of acetonitrile with 2-ethoxyethanol/2-butoxyethanol due to cross association between these dissimilar molecules [8]. V_m^E becomes more negative with increase in temperature. This indicates that thermal energy activates unlike molecules towards complex formation through H-bonding. Negative trends in V_m^E have also been reported for binary mixtures of ethylene glycol + water [9].

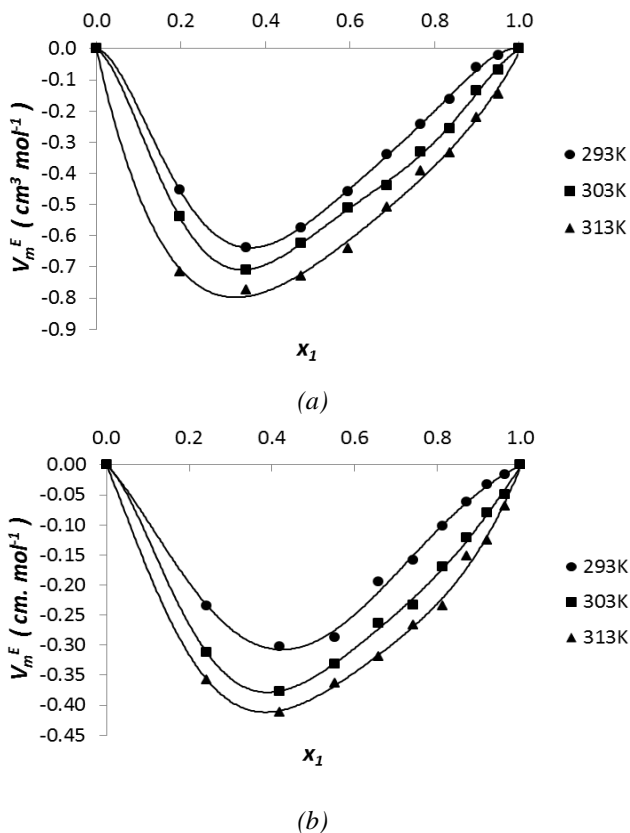


Figure 1: Excess molar volume (V_m^E) vs. mole fraction of acetonitrile (x_1) for binary mixtures (a) acetonitrile + 2-ethoxyethanol and (b) acetonitrile + 2-butoxyethanol at varying temperatures

The positive values of deviation in ultrasonic velocity (Δu) reflect strong specific interaction between unlike molecules. The sign and magnitude of Δu play an important

role in describing molecular rearrangement as a result of molecular interaction between component molecules in the liquid mixtures. It has been noticed from fig. 2 that Δu has positive values for acetonitrile + 2-ethoxyethanol and acetonitrile + 2-butoxyethanol binary mixtures over whole composition range at temperatures 293K, 303K and 313K respectively. A similar behavior of Δu has also been observed for binary mixtures of acetophenone+ benzene by Sarvankumar et.al [10]. It can also be observed from fig. 2 that interaction is stronger in case of acetonitrile + 2-ethoxyethanol mixture when compared with acetonitrile + 2-butoxy ethanol. The positive values of Δu increase with increase in temperature which indicates the increase in strength of interaction with temperature in both the mixtures. observed for binary mixtures of acetophenone+ benzene by Sarvankumar et.al [10]. It can also be observed from fig. 2 that interaction is stronger in case of acetonitrile + 2-ethoxyethanol mixture when compared with acetonitrile + 2-butoxy ethanol. The positive values of Δu increase with increase in temperature which indicates the increase in strength of interaction with temperature in both the mixtures.

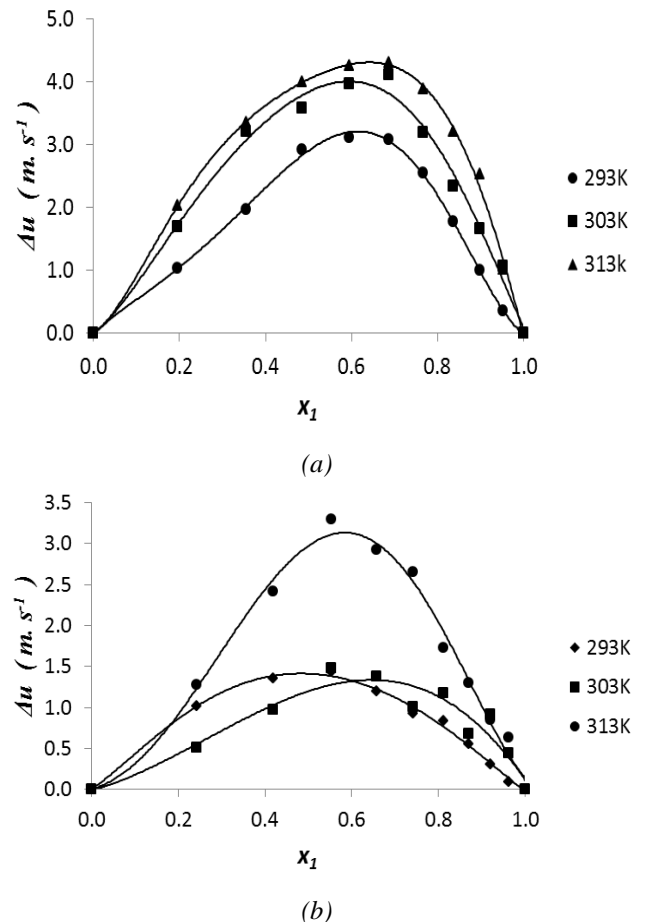


Figure 2: Deviation in ultrasonic velocity (Δu) vs. mole fraction of acetonitrile (x_1) for binary mixtures (a) acetonitrile + 2-ethoxyethanol and (b) acetonitrile + 2-butoxyethanol at varying temperatures

It can be seen from figs. 3 that the values of deviation in isentropic compressibility (Δk_s) for both the mixtures have been found to be negative over the entire composition range at all the temperatures studied here. The negative values of Δk_s suggest that the mixture is less compressible than the corresponding ideal mixtures [11, 12].

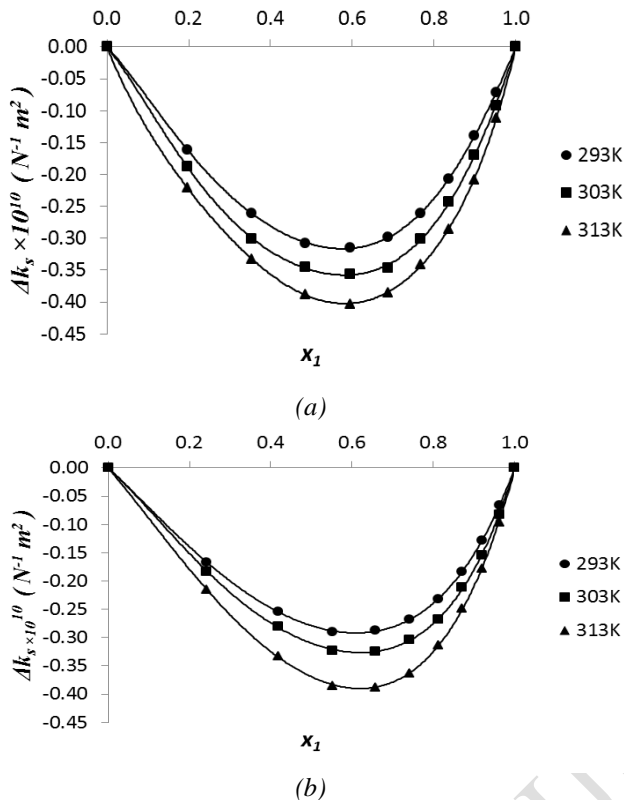


Figure 3: Deviation in isentropic compressibility (Δk_s) vs. mole fraction of acetonitrile (x_1) for binary mixtures (a) acetonitrile + 2-ethoxyethanol and (b) acetonitrile + 2-butoxyethanol at varying temperatures

The observed values of Δk_s for these mixtures can be explained as a result of cumulative manifestation of various types of intermolecular interactions between the components. The order of negative values of deviation in isentropic compressibility (Δk_s) for acetonitrile + 2-ethoxyethanol is greater than acetonitrile + 2-butoxyethanol mixture, which suggests that interaction between acetonitrile + 2-ethoxyethanol mixture is stronger as compared to acetonitrile + 2-butoxyethanol mixture. The magnitude of Δk_s values increases with an increase in temperature for both the mixtures which suggests that thermal energy enhances the strength of intermolecular interaction [13, 14].

The values of co-efficient a_i evaluated using the method of least squares for both the mixtures are given in table 2 and 3 along with the standard deviations $\sigma(Y^E)$.

Parameters	Temp. (K)	a_1	a_2	a_3	a_4	a_5	$\sigma(Y^E)$
acetonitrile+ 2-ethoxyethanol							
V_m^E	293	-2.2452	-1.9617	-0.5510	1.7752	2.7859	0.0099

$(cm^3.mol^{-1})$	303	-2.4361	-1.5103	-4.1251	1.7103	7.9379	0.0105
	313	-2.8960	-1.4304	-0.1206	-1.1394	3.4072	0.0144
Δu ($m.s^{-1}$)	293	10.9412	-10.3118	-0.1595	11.9274	5.3254	0.0610
	303	14.7948	-6.7269	17.0378	-10.6603	27.9143	0.1353
	313	16.0722	-3.6275	-1.3509	-15.4460	21.7711	0.0316
$\Delta k_s \times 10^{10}$ ($N^{-1}.m^2$)	293	-1.2406	0.3531	-0.1282	0.1321	0.3434	0.0015
	303	-1.7013	1.0671	1.6034	1.5757	-2.7491	0.0023
	313	-1.5682	0.4832	-0.3075	-0.0278	-0.0442	0.0017
$K_s^E \times 10^4$ ($m^5.N^{-1}.mol^{-1}$)	293	40.6833	-10.7446	-1.1874	14.9583	34.1709	0.1485
	303	51.2728	-29.5216	-7.4860	47.7037	19.4448	0.2110
	313	-67.2769	-9.4584	-8.1496	-0.5060	-59.7938	0.2162

Table 2: Adjustable parameters a_i with the standard deviations $\sigma(Y^E)$ for excess molar volume (V_m^E), deviation in ultrasonic velocity (Δu), deviation in isentropic compressibility (Δk_s) and excess molar compressibility (K_s^E) for binary mixture of acetonitrile + 2-ethoxyethanol at temperature 293, 303 and 313K

Parameters	Temp. (K)	a_1	a_2	a_3	a_4	a_5	$\sigma(Y^E)$
acetonitrile+ 2-ethoxyethanol							
V_m^E ($cm^3.mol^{-1}$)	293	-2.0939	-2.5780	2.8579	7.9540	4.3020	0.0119
	303	-2.2335	3.6516	5.4478	-12.9028	-14.5447	0.0075
	313	-1.5453	-0.8091	-0.8044	1.3194	0.7331	0.0121
Δu ($m.s^{-1}$)	293	5.3652	1.3873	4.6178	-5.6749	-14.0910	0.0594
	303	6.7894	-2.1584	11.3060	10.9258	29.2125	0.0653
	313	6.7412	-1.0846	1.2684	-1.8231	9.8573	0.0269
$\Delta k_s \times 10^{10}$ ($N^{-1}.m^2$)	293	1.3387	-0.1377	0.2892	2.3904	1.3894	0.0012
	303	-1.2423	0.5805	-0.1164	0.0952	-0.4745	0.0020
	313	-1.4808	0.7101	-0.0332	0.0057	-0.7411	0.0016
$K_s^E \times 10^{14}$ ($m^5.N^{-1}.mol^{-1}$)	293	-8.6468	-29.2683	23.3046	83.1458	82.1744	0.1836
	303	15.9777	10.6125	31.5835	-36.8310	-79.2213	0.1536
	313	14.9008	3.2558	7.7671	1.5659	-31.0364	0.1806

Table 3: Adjustable parameters a_i with the standard deviations $\sigma(Y^E)$ for excess molar volume (V_m^E), deviation in ultrasonic velocity (Δu), deviation in isentropic compressibility (Δk_s) and excess molar compressibility (K_s^E) for binary mixture of acetonitrile + 2-butoxyethanol at temperature 293, 303 and 313K

IV. CONCLUSIONS

The observed values and their excess parameters suggest weak dipole-dipole interaction and dispersive force may contribute in result of density and velocity and their excess values.

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