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Title Key: Excess Thermodynamic Properties of Binary Liquid Mixtures

Excess Thermodynamic Properties of Binary Liquid Mixtures of DMSO with Methanol at Different Temperatures

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Abstract

In the present studyattempt has been made to determine acoustic and thermodynamic parameters for binary liquid mixture of DMSO with methanol at 295.15 K, 300.15 K, 305.15 K, 310.15 K and 315.15 K temperatures. The excess values of isentropic compressibility, acoustic impedance, and internal pressure have been calculated using experimental data of ultrasonic velocity, density and viscosity. Molecular interactions in mixture form have been discussed depending upon deviations in excess values. Experimental data have been validated using Redlich-Kister polynomial equation.

KeywordsAvailable volume, binary, excess isentropic compressibility, Redlich-Kister, specific acoustic impedance.

1. Introduction

Molecular interaction studies in liquids and liquid mixtures are highly applicable in a number of fields such as food processing, drugs industries, pharmaceuticals, petroleum industries, paint industries, fluid mechanics etc. Various experimental methods have been used to investigate the interactions between the components of liquid mixtures. It has been found that there is concrete need of thermodynamic data not only for researchers but also for industries to design and set up. This is the reason; many researchers have been approached to continue the study in this area [1 to27]. In industries, for the processing and product formulation liquid binary mixtures are mainly used instead of pure liquids as a part of industrial application [20].

In the present study experimental values of ultrasonic velocity, density and viscosity have been obtained for pure dimethyl Sulfoxide and methanol, and their binary liquid mixtures at temperatures from 298.15 K to 315.15 K with interval of 5 K temperature. From these values excess parameters have been calculated. The parameters like excess intermolecular free length, excess Gibb's free energy of activation, excess molar volume

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have been published earlier [21-23]. In the present research paper, attempt has been made to explain intermolecular interactions in binary liquid mixtures with the help of deviation in excess values of isentropic compressibility, acoustic impedance, and internal pressure. As per the increasing demand for accuracy to explicit the study of binary liquid mixtures, data has been validated by means of several theoretical as well as semi empirical equations.

2. Materials and Methods

Details of the materials used for the investigation as well as experimental methods have been already discussed [21-23]. Using experimental data isentropic compressibility have been determined using relation

$$K_s = \frac{1}{U^2\rho} \quad \ldots\ldots\ldots\ldots (1)$$

Where, K_s, U and ρ are isentropic compressibility, ultrasonic velocity and density of the medium.

The formula used for the determination of acoustic impedance (Z) is

$$Z = \rho \times U \quad \ldots\ldots\ldots\ldots (2)$$

Internal pressure have been determined using the relation

$$\pi_i = bRT\left[\frac{k\eta}{U}\right]^{\frac{1}{2}} \frac{\rho^{\frac{2}{3}}}{M^{\frac{7}{6}}} \quad \ldots\ldots\ldots\ldots (3)$$

Where, π_i is internal pressure, b is packing factor in liquid, T is absolute temperature, k is equal to 4.28 $\times 10^9$, which is temperature independent constant, η is viscosity, ρ is density, U is ultrasonic velocity and M is effective molecular mass.

The nature of molecular agitation in dissimilar molecules and thus molecular interactions is well understood by studying excess parameters. Deviation of thermodynamic parameter from ideal value is quantitatively measured in terms of excess value [6]. Excess values have been calculated by using relation,

$$A^E = A_{Exp} - \sum x_i A_i \quad \ldots\ldots\ldots\ldots (4)$$

Where, A_E is the excess value and A_{Exp} is experimental measured value of parameter, X_i and A_i are mole fraction and value of parameter for i^{th} component respectively.

3. Results

From experimental data of density, viscosity and ultrasonic velocity, thermodynamic parameters have been evaluated such as isentropic compressibility, acoustic impedance and internal pressure. Calculated results have been listed in table1.

Coefficients of Redlich-Kister polynomial equation [27] with standard deviations (a_i and σ) for DMSO with methanol at all temperatures have been listed in table 2.

Using equation (4), the excess values of the parameters listed in table1 are calculated and represented in the form of graphs (1, 2 and 3)

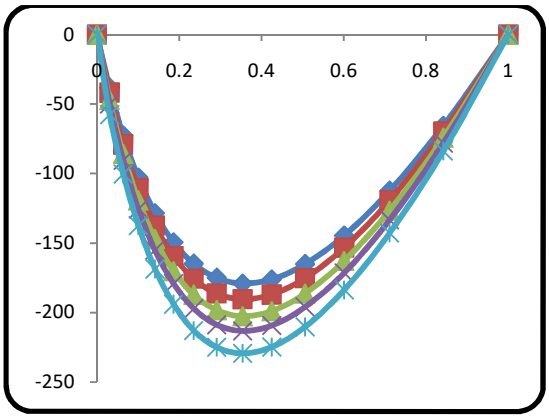

Figure 1 Plot of excess isentropic compressibility against mole fraction of DMSO

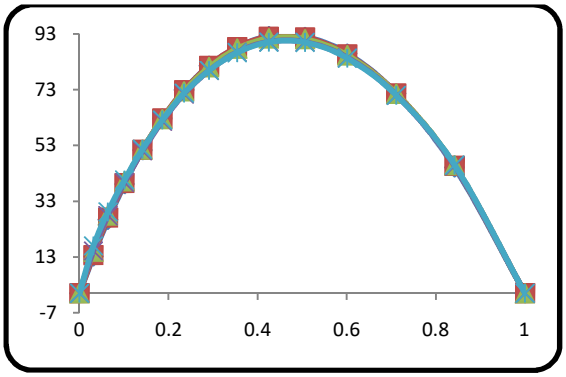

Figure 2 Plot of acoustic impedance against mole fraction of DMSO

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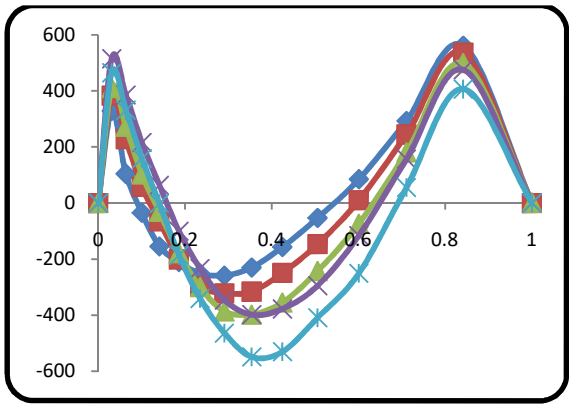

Figure 3 Plot of excess internal pressure against mole fraction of DMSO

4. Discussions and Conclusions

The values of excess isentropic compressibility have been found negative over entire concentration range at all temperatures. It becomes more negative as temperature increases. The deviation in excess acoustic impedance if found to be positive for all temperatures and at ide concentrations. As concentration of DMSO increases in the mixture, Z^E initially increases, become maximum at mole fraction in the range of 0.4 to 0.6, and then decreases as concentration of DMSO is further increased. The values of excess internal pressure have been noticed with both positive as well as negative trends for all temperatures. The values of standard deviation for isentropic compressibility using theoretical relation given by Redlich-Kister give validation of experimental results.

Upon adding the liquids, increase or decrease in hydrogen bonding in the mixture may affect deviation in the values of excess parameters with respect temperature as well as composition. Adhesive or cohesive forces causing molecular interactions have been noticed as an effect of deviation in excess parameters [7]. The structural arrangements of molecules including their shape are greatly affected by molecular interactions [8].

Systematic evaluation of thermodynamic parameters and their excess values have been carried out. Using semi empirical Redlich-Kister equation, validation of isentropic compressibility has been carried out satisfactorily. It has been concluded that negative deviation in excess isentropic compressibility, positive deviation in acoustic impedance tends to give stronger interactions between hetero molecules in the liquid mixture at all temperatures.

5. Acknowledgements

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X1↓	Isentropic Compressibility ($k_s \times 10^2$)					Acoustic Impedance ($Z \times 10^{-3}$)					Internal Pressure ($\pi_i \times 10^3$)				
Temp. →	T1	T2	T3	T4	T5	T1	T2	T3	T4	T5	T1	T2	T3	T4	T5
0.000	10.0	10.5	10.9	11.4	11.9	884.5	863.9	843	823.8	802	1.05	1.04	1.03	1.01	1.02
0.031	9.51	9.89	10.2	10.7	11.1	920.9	900.6	880.7	861.6	841.5	1.07	1.07	1.06	1.06	1.05
0.064	8.96	9.31	9.68	10.0	10.4	959.3	939.1	918.6	899.1	878.3	1.04	1.04	1.04	1.03	1.03
0.101	8.44	8.76	9.10	9.46	9.85	999.7	979	958.2	938.0	916.8	1.02	1.01	1.01	1.00	1.00
0.141	7.94	8.24	8.56	8.88	9.24	1042	1021	999.8	979.2	957.5	0.99	0.99	0.98	0.97	0.97
0.186	7.47	7.74	8.03	8.33	8.65	1087	1066	1044	1022	1000	0.97	0.96	0.95	0.94	0.93

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0.235	7.01	7.26	7.53	7.80	8.10	1135	1113	1091	1069	1047	0.95	0.93	0.92	0.91	0.90
0.291	6.58	6.80	7.05	7.29	7.56	1186	1164	1141	1119	1096	0.94	0.91	0.90	0.88	0.86
0.354	6.16	6.37	6.58	6.81	7.06	1240	1218	1194	1171	1148	0.92	0.89	0.87	0.85	0.83
0.425	5.76	5.95	6.15	6.35	6.57	1298	1275	1251	1228	1205	0.91	0.88	0.85	0.83	0.81
0.506	5.38	5.55	5.73	5.92	6.11	1359	1336	1312	1288	1265	0.89	0.86	0.84	0.81	0.80
0.601	5.02	5.17	5.33	5.50	5.68	1425	1401	1377	1352	1328	0.88	0.85	0.82	0.80	0.77
0.711	4.68	4.82	4.96	5.11	5.26	1494	1470	1445	1421	1397	0.87	0.84	0.81	0.79	0.76
0.842	4.36	4.48	4.61	4.74	4.88	1567	1542	1518	1492	1468	0.85	0.82	0.83	0.77	0.75
1.000	4.07	4.18	4.30	4.42	4.55	1641	1615	1590	1564	1539	0.75	0.72	0.70	0.67	0.65

Table 1 Isentropic compressibility, Acoustic impedance and Internal pressure values for binary liquid mixture of DMSO and Methanol at T1 T2, T3, T4 and T5 temperatures

T(K)	a_0	a_1	a_2	a_3	a_4	Σ
DMSO + Methanol						
295.15	-665.61	339.44	-171.51	115.75	-81.39	0.1142
300.15	-707.37	362.18	-164.89	131.04	-140.46	0.3344
305.15	-756.88	390.11	-87.20	134.20	-333.27	1.2786
310.15	-797.98	411.40	-73.82	138.33	-385.55	1.5780
315.15	-864.43	452.33	56.84	141.66	-700.00	3.2985

Table 2Coefficients of Redlick-Kister and standard deviation for binary liquid mixture of DMSO and methanol

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