Acoustical Studies on Molecular Interactions in Binary Liquid Mixtures at 303 K

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Abstract: Molecular interaction studies using ultrasonic technique in the binary liquid mixtures of cyclohexanone with *o*-cresol and *p*-cresol have been carried out at 303 K. Using the measured values of ultrasonic velocity, density and viscosity, acoustical parameters and their excess values are evaluated. From the properties of these excess parameters the nature and strength of the interactions in these binary systems are discussed.

Keywords: Ultrasonic velocity, Acoustical parameters, Binary mixtures.

Introduction

In recent years, ultrasonic technique has become a powerful tool for studying the molecular behaviour of liquid mixtures¹⁻³. This is because of its ability of characterizing physico-chemical behaviour of liquid medium⁴⁻⁶. The measurement of ultrasonic velocity have been adequately employed in understanding the molecular interactions in liquid mixtures. Molecular interaction studies can be carried out by both spectroscopic^{7,8} and non-spectroscopic^{9,10} techniques. However, ultrasonic velocity¹¹ and viscosity¹² measurements have been widely used in the field of interactions and structural aspect evaluation studies.

Experimental

The ultrasonic velocity was measured at 303 K using a single crystal interferometer with a high degree of accuracy operating at a frequency of 2 MHz. The density was measured at 303 K using specific gravity bottle by the standard procedure and the viscosity was measured at 303 K using Ostwald's viscometer with an accuracy of $\pm 0.001 \text{ Nsm}^{-2}$.

Results and Discussion

The acoustical parameters such as adiabatic compressibility (β), free length (L_f) and free volume (V_f) were calculated using the following relations,

$$\beta = 1/U^2 \rho \quad (1)$$

$$L_f = k(\beta)^{1/2} \quad (2)$$

$$V_f = (M_{\text{eff}} U / \eta k)^{3/2} \quad (3)$$

The excess values are calculated using the formula,

$$A^E = A_{\text{exp}} - A_{\text{id}} \quad (4)$$

Where, $A_{\text{id}} = \sum A_i X_i$, where A_i is any acoustical parameter and X_i is the mole fraction of liquid component.

Table 1 shows the values of ultrasonic velocity (U), density (ρ), viscosity (η) and excess adiabatic compressibility (β^E), excess free length (L_f^E), excess free volume (V_f^E) for cyclohexanone + *o*-cresol, *p*-cresol at 303 K. From the Table 1, it is observed that as the concentration of cyclohexanone increases the ultrasonic velocity decreases for both the systems studied.

As shown in Table 1, β^E values are negative which suggest the presence of hydrogen bonding interaction between the components of the liquid mixtures. However, β^E values are less negative for the *o*-cresol system than that of *p*-cresol system. This indicates that the less interaction in the former system. The possible reason may be as follows, in *o*-cresol, the closeness of $-\text{CH}_3$ to $-\text{OH}$ group shows the presence of two types of effect. One is the increase of electron density in the O–H bond and the other is the steric effect. These two effects decrease the strength of the intermolecular hydrogen bond formation in *o*-cresol than in *p*-cresol¹³.

Table 1. Experimental values of ultrasonic velocity (U), density (ρ), viscosity (η) and excess values of adiabatic compressibility (β^E), free length (L_f^E), free volume (V_f^E) for cyclohexanone + *o*-cresol, *p*-cresol at 303 K.

X_1	U ms^{-1}	ρ kg m^{-3}	η $\times 10^{-3} \text{ Nsm}^{-2}$	β^E $\times 10^{-11} \text{ N}^{-1} \text{m}^2$	L_f^E , $\times 10^{-12} \text{ m}$	V_f^E $\times 10^{-7} \text{ m}^3 \text{mol}^{-1}$
Cyclohexanone + <i>o</i> -cresol						
0.1999	1465.8	1014.4	6.265	-0.424	-0.146	-0.074
0.4000	1445.3	994.8	5.227	-0.506	-0.156	-0.124
0.5000	1436.9	984.6	4.472	-0.599	-0.193	-0.126
0.6000	1425.1	972.6	3.853	-0.318	-0.069	-0.121
0.8002	1402.9	955.7	2.913	-0.101	-0.003	-0.090
Cyclohexanone + <i>p</i> -cresol						
0.1998	1454.2	1007.8	8.734	-0.528	-0.205	-0.065
0.4001	1443.7	991.5	5.878	-1.095	-0.438	-0.104
0.4998	1435.2	981.2	4.818	-1.017	-0.397	-0.108
0.6002	1424.3	972.4	4.003	-0.826	-0.311	-0.104
0.8000	1404.2	953.5	2.898	-0.356	-0.118	-0.070

The intermolecular free length L_f has been calculated by using semi-empirical relation given by Jacobson¹⁴. Since L_f is a derived parameter from β , the trends in the variation of L_f^E exhibit more or less similar pattern as that of β^E values. In general, system exhibiting specific interactions, the free length should decrease resulting in negative L_f^E values. From Table 1, it is observed that L_f^E and V_f^E values are negative at all concentrations which indicate the existence of intermolecular interactions between the components¹⁵.

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