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# Molecular interaction studies on n-alkanols in cyclohexane with DMF at 303 k

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## Abstract

The ultrasonic velocity, density and viscosity have been measured for the mixtures for the ternary system of n–alkanols, namely, 1–propanol, 1–butanol, and 1–pentanol in cyclohexane with N- N dimethyl formamide (DMF) at 303K. From these data, some of the acoustical parameter such as adiabatic compressibility ($\beta$), freelength ($L_f$), free volume ($V_f$) and internal pressure ($\pi_i$) have been measured. The excess values of the above parameters are also evaluated and presented. The results have been analysed and interpreted in terms of molecular association such as hydrogen bonding formed between 1-alkanol and DMF. Further, such addition of DMF makes dissociation of associated structure of 1-alkanols. The observed excess values predict weak interactions in the present systems

**Keywords:** adiabatic compressibility, free length, free volume, internal pressure, dipole-dipole interaction, hydrogen bonding.

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## Introduction

Ultrasonic investigations of liquid mixtures consisting of polar and non-polar components are of considerable importance in understanding intermolecular interactions between the component molecules and they find applications in several industrial and technological processes [1,2]. Further, such studies as functions of concentration are useful in gaining insight into the structure and bonding of associated molecular completes and other molecular processes. Further, the variation of ultrasonic velocity and other ultrasonic parameters along with their excess values of binary or ternary liquid mixtures with changing mole fraction of one of the components has been investigated by many researchers [3,4].

The study of molecular association in organic ternary mixtures having alcohol as one of the components is of particular interest, since alcohols are strongly self-associated liquid having a three dimensional network of hydrogen bond [5] and can be associated with any other group having some degree of polar attractions [4]. Although, several investigations [6-8] were carried out in liquid mixtures having alcohol as one of the components, a systematic study in a series of primary alcohols in ternary systems has been scarcely reported. An exhaustive study of literature has shown that a few attempts have been made for the ultrasonic velocity data for ternary mixtures [9-12]. Hence, authors has taken the ternary liquid mixture of 1- alkanols in cyclohexane with DMF at 303k.

## Materials and Methods

In all systems, the mole fraction of the second component, cyclohexance ($X_2$ = 0.4) was kept fixed while the mole fractions of the remaining two were varied from 0.0 to 0.6 so as to have the mixtures of different compositions. There is nothing significant on fixing the second component at $X_2$=0.4. The ultrasonic velocity in liquid mixtures have been measured using an ultrasonic interferometer Mittal Enterprises,: (Model: F81) working at frequency 3MHz with an overall accuracy of ± 2 $ms^{-1}$. The density of liquid and liquid mixtures were measured with a specific gravity bottle of 5 ml capacity with an accuracy of ± 0.1mg. An Ostwald's Viscometer of 10 ml capacity with an accuracy of ± 0.001 $Nsm^{-2}$ used for viscosity measurements. All the precautions were taken to minimise the possible experimental error. The values obtained are compared with literature and found that they makes very well with each other.

### *Theory*

The following acoustical parameters have been evaluated.

The Adiabatic compressibility (β)

$$\beta = \frac{1}{U^2\rho}$$

where U- ultrasonic velocity and $\rho$ - density …(1)

Intermolecular freelength ($L_f$)

$$L_f = K_T\sqrt{\beta} \quad \text{…(2)}$$

where $\beta$ - adiabatic compressibility and $K_T$ is a temperature dependent constant.

Free volume ($V_f$)

$$V_f = \left(\frac{M_{eff}U}{K\eta}\right)^{3/2} \quad \text{…(3)}$$

where $M_{eff}$ is the effective molecular weight ( $M_{eff} = \Sigma m_i x_i$, in which $m_i$ and $x_i$ are the molecular weight and the mole fraction of the individual constituents respectively). K is a temperature independent constant which is equal to 4.28 × $10^9$ for all liquids.

The internal pressure can be found out as

$$\pi_i = bRT\left(\frac{K\eta}{U}\right)^{1/2}\left(\frac{\rho^{2/3}}{M_{eff}^{7/6}}\right) \qquad \ldots(4)$$

K is a constant, T the absolute temperature, η the viscosity in $Nsm^{-2}$, U the ultrasonic velocity in $ms^{-1}$, ρ the density in $Kgm^{-3}$, $M_{eff}$ the effective molecular weight.

The Excess parameter ($A^E$) has been calculated by using the relation

$$A^E = A_{\exp} - A_{id} \qquad \ldots(5)$$

where $A_{id} = \sum_{i=1}^{n} A_i X_i$ , $A_i$ is any acoustical parameters and $X_i$ the mole fraction of the liquid component.

## Results and Discussion

The present systems taken up for study at 303K are:

| | |
|---|---|
| System – I | 1-propanol + cyclohexane + DMF |
| II | 1-butanol + cyclohexane + DMF |
| III | 1-pentanol + cyclohexane + DMF |

The experimentally determined values of density (ρ), viscosity (η) and ultrasonic velocity (U) at 303K for the ternary liquid systems (I – III) is given in Table-1. The values of adiabatic compressibility (β), freelength ($L_f$), free volume ($V_f$), and internal pressure ($\pi_i$) at 303K are given in Table-2. The excess values of excess adiabatic compressibility ($\beta^E$), excess free length ($L_f^{\ E}$), excess free volume ($V_f^{\ E}$), and excess internal pressure( $\pi_i^E$) has been evaluated and are reported in Table-3.

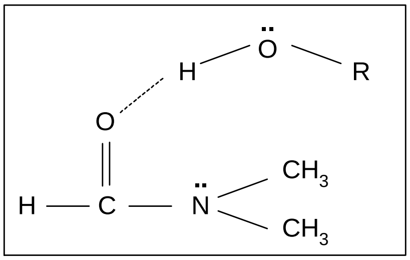
**Table-1 The values of density (ρ), viscosity (η) and ultrasonic velocity (U) at 303K**

| $X_1$ | $X_3$ | Density ρ/(kg/m$^3$) | Viscosity η/(×10$^{-3}$ NSm$^{-2}$) | Velocity U/(m/s) |
|---|---|---|---|---|
| **System I: 1-propanol + cyclohexane + DMF** | | | | |
| 0 | 0.6000 | 776.76 | 1.0238 | 1184.9 |
| 0.1000 | 0.4999 | 791.72 | 0.9118 | 1206.0 |
| 0.2000 | 0.3999 | 799.94 | 0.8518 | 1221.6 |
| 0.3000 | 0.2999 | 817.82 | 0.8029 | 1241.1 |
| 0.3999 | 0.2000 | 831.59 | 0.7992 | 1269.6 |
| 0.4999 | 0.1000 | 845.28 | 0.7661 | 1289.2 |
| 0.5998 | 0 | 871.00 | 0.6465 | 1301.2 |
| **System II: 1-butanol + cyclohexane + DMF** | | | | |
| 0 | 0.6000 | 783.18 | 1.2016 | 1199.3 |
| 0.1000 | 0.5000 | 796.31 | 1.0884 | 1204.3 |

| | | | | |
|---|---|---|---|---|
| 0.2000 | 0.3999 | 805.01 | 0.9769 | 1238.9 |
| 0.2999 | 0.3000 | 815.45 | 0.8954 | 1255.8 |
| 0.4000 | 0.2000 | 828.47 | 0.8089 | 1263.7 |
| 0.4999 | 0.1000 | 831.75 | 0.7489 | 1271.8 |
| 0.6000 | 0 | 838.17 | 0.6994 | 1282.4 |
| **System III: 1-pentanol + cyclohexane + DMF** | | | | |
| 0 | 0.6000 | 789.2410 | 1.4803 | 1224.6 |
| 0.1000 | 0.4999 | 790.7700 | 1.2389 | 1233.7 |
| 0.2021 | 0.3989 | 806.4602 | 1.0932 | 1245.5 |
| 0.2978 | 0.2978 | 818.1537 | 0.9573 | 1256.2 |
| 0.4000 | 0.1999 | 825.6045 | 0.8726 | 1274.1 |
| 0.5000 | 0.0998 | 839.3677 | 0.8186 | 1291.6 |
| 0.5771 | 0 | 845.1700 | 0.7087 | 1304.7 |

In all the three liquid systems, the ultrasonic velocity increases with increasing concentration of 1-alkanols. It is observed that as the number of hydrocarbon group increases, which lead to increase in ultrasonic velocity. This behaviour at such concentrations which is different from the ideal mixture behaviour can be attributed to intermolecular interactions in the systems studied [13-16]. The adiabatic compressibility($\beta$) and intermolecular freelength ($L_f$) also increases with increase of alkanol concentrations. Such a continuous increase in adiabatic compressibility with respect to the solute concentration has been qualitatively ascribed to the effect of hydrogen bonding or dipole-dipole interactions [17].

N-N dimethylformamide (DMF) is a non-aqueous solvent of particular interest, because it has no hydrogen bonding in pure state. Therefore, it acts as an aprotic protophilic medium with high dielectric constant and it is considered as a dissociating solvent [4].



Further, mixing of such DMF with 1-alkanols causes dissociation of hydrogen bonded structure of 1-alkanols and subsequent formation of (new) H-bond (C = O … H –O) between proton acceptor oxygen atom (with lone pair of electrons) of C=O group of DMF and hydrogen atom of –OH group of 1-alkanol molecules. This dissociation effect leads to an decrease in volume and hence an increase in adiabatic compressibility. Further, the molecules of alkanols are self-associated in pure state through hydrogen bonding. However mixing of DMF with alkanols would release the dipoles [18] of alkanols and interact with DMF molecules forming strong hydrogen bonds, leading to contraction in volume[17] which makes an increase in free length. Such an increase in free length may also be attributed due to the loose packing of molecules inside the shield, which may be brought by weakening of molecular interactions [19].

Further, cyclohexane belongs to alicyclic hydrocarbon (closed chain). The packing of carbon atoms in this even numbered alkane group allows the maximum intermolecular attractions [20] and therefore these molecules are highly inert towards an electrophile or nucleophile at ordinary temperature. In the present study, among the three components, cyclohexane is not expected to involve in any interactions either with DMF or with 1-alkanols due to its non-polar nature. As the concentration of alkanols increases in all the three systems, it is suggested that effect due to rupture of hydrogen bonded associates of alkanols dominate over that H-bonding between unlike molecules. i.e DMF-alkanols interaction is weaker than DMF-DMF and alkanol-alkanol interaction [21] which causes a decrease in free volume. As the dipole moment of Cyclohexane is zero [22] the decrease in free volume shows that the molecular interactions are may be due to H-bonding or dipole-dipole induced.

**Table-2 The values of adiabatic compressibility (β), free length ($L_f$) free volume ($V_f$) and internal pressure ($\pi_i$) at 303K**

| $X_1$ | $X_3$ | Adiabatic compressibility $\beta/(\times10^{-10}\,m^2\ N^{-1})$ | Free length $L_f/(\times\ 10^{-10}\,m)$ | Free volume $V_f/(\times10^{-7}m^3\ mol^{-1})$ | Internal pressure $\pi_i/(\times10^{6}\ Nm^{-2})$ |
|---|---|---|---|---|---|
| **System I: 1-propanol + cyclohexane + DMF** | | | | | |
| 0 | 0.6000 | 6.7809 | 0.5196 | 2.2008 | 418.6408 |
| 0.1000 | 0.4999 | 7.1180 | 0.5323 | 1.6404 | 457.7283 |
| 0.2000 | 0.3999 | 7.4603 | 0.5450 | 1.4662 | 475.4544 |
| 0.3000 | 0.2999 | 7.9383 | 0.5622 | 1.3711 | 486.4344 |
| 0.3999 | 0.2000 | 8.3769 | 0.5775 | 1.1927 | 508.1781 |
| 0.4999 | 0.1000 | 8.6843 | 0.5880 | 1.0282 | 536.6859 |
| 0.5998 | 0 | 9.1696 | 0.6042 | 0.8182 | 579.0633 |
| **System II: 1-butanol + cyclohexane + DMF** | | | | | |
| 0 | 0.6000 | 7.2547 | 0.5374 | 1.9135 | 427.5290 |
| 0.1000 | 0.5000 | 7.4331 | 0.5440 | 1.7194 | 439.2925 |
| 0.2000 | 0.3999 | 7.5585 | 0.5486 | 1.5107 | 458.2339 |
| 0.2999 | 0.3000 | 7.7761 | 0.5564 | 1.2878 | 477.7979 |
| 0.4000 | 0.2000 | 8.0933 | 0.5676 | 1.1095 | 497.3565 |
| 0.4999 | 0.1000 | 8.6586 | 0.5871 | 0.9060 | 527.8032 |
| 0.6000 | 0 | 8.8773 | 0.5945 | 0.7778 | 548.7623 |
| **System III: 1-pentanol + cyclohexane+ DMF** | | | | | |
| 0 | 0.6000 | 6.9508 | 0.5260 | 1.9253 | 429.0284 |
| 0.1000 | 0.4999 | 7.1415 | 0.5332 | 1.5726 | 451.0483 |
| 0.2021 | 0.3989 | 7.4614 | 0.5450 | 1.4408 | 453.4930 |
| 0.2978 | 0.2978 | 7.7451 | 0.5553 | 1.2618 | 465.3756 |
| 0.4000 | 0.1999 | 7.9933 | 0.5641 | 1.0488 | 484.3796 |
| 0.5000 | 0.0998 | 8.3089 | 0.5751 | 0.8801 | 500.8843 |
| 0.5771 | 0 | 8.4489 | 0.5800 | 0.6832 | 538.3118 |

Further, a decrease in free volume and an increase in internal pressure with increase in concentrations of 1-alkanols is observed which may be attributed to increasing magnitude of interactions [23]. The increase in internal pressure also indicates association through hydrogen bonding [24] and hence supports the present investigation. Similar results were observed by [25].

In order to understand the nature of molecular interactions between the components of the liquid mixtures, it is of interest to discuss the same in terms of excess parameter rather than actual values. Non-ideal liquid mixtures show considerable deviation from linearity in their physical behaviour with respect to concentration and these have been interpreted as arising from the presence of strong or weak interactions. The effect of deviation depends upon the nature of the constituents and composition of the mixtures.

**Table-3 The Excess values of adiabatic compressibility ($\beta^E$), free length ($L_f^E$) free volume ($V_f^E$) and internal pressure ($\pi_i$) at 303K**

| $X_1$ | $X_3$ | Excess Adiabatic compressibility $\beta^E/(\times10^{-10}\,m^2\,N^{-1})$ | Excess Free length $L_f^E\,/(\times10^{-10}\,m)$ | Excess Free volume $V_f^E\,/(\times10^{-7}m^3\,mol^{-1})$ | Excess Internal pressure $\pi_i^E\,/(\times10^6\,Nm^{-2})$ |
|---|---|---|---|---|---|
| **System I: 1-propanol + cyclohexane + DMF** | | | | | |
| 0 | 0.6000 | 0.2993 | 0.0100 | 0.0486 | -1.1124 |
| 0.1000 | 0.4999 | 0.1962 | 0.0083 | 0.1047 | -1.1523 |
| 0.2000 | 0.3999 | 0.2746 | 0.0125 | 0.1156 | -1.0514 |
| 0.3000 | 0.2999 | 0.2201 | 0.0333 | 0.1406 | -0.8836 |
| 0.3999 | 0.2000 | 0.1273 | 0.0358 | 0.0820 | -0.6079 |
| 0.4999 | 0.1000 | 0.1698 | 0.0339 | 0.1026 | -0.3996 |
| 0.5998 | 0 | 0.2171 | 0.0130 | 0.5091 | -0.4053 |
| **System II: 1-butanol + cyclohexane + DMF** | | | | | |
| 0 | 0.6000 | 0.3836 | 0.0131 | 0.0252 | -88.6188 |
| 0.1000 | 0.5000 | 0.4865 | 0.0255 | 0.0032 | -79.8413 |
| 0.2000 | 0.3999 | 0.2429 | 0.0111 | 0.0439 | -80.6224 |
| 0.2999 | 0.3000 | 0.2481 | 0.0325 | 0.0657 | -70.4021 |
| 0.4000 | 0.2000 | 0.3518 | 0.0171 | 0.1323 | -60.2948 |
| 0.4999 | 0.1000 | 0.5476 | 0.0249 | 0.1842 | -49.5833 |
| 0.6000 | 0 | 0.6908 | 0.0308 | 0.2219 | -31.6457 |
| **System III: 1-pentanol + cyclohexane+ DMF** | | | | | |
| 0 | 0.6000 | 0.2314 | 0.0083 | 0.0807 | -53.8210 |
| 0.1000 | 0.4999 | 0.3852 | 0.0149 | 0.0170 | -74.5808 |
| 0.2021 | 0.3989 | 0.3411 | 0.0146 | 0.0073 | -67.8648 |
| 0.2978 | 0.2978 | 0.3551 | 0.0162 | 0.0453 | -62.8389 |
| 0.4000 | 0.1999 | 0.3515 | 0.0169 | 0.0697 | -52.7661 |
| 0.5000 | 0.0998 | 0.3053 | 0.0159 | 0.0399 | -31.3896 |
| 0.5771 | 0 | 0.3869 | 0.0195 | 0.2336 | -30.1464 |

In the present investigation, the excess adiabatic compressibility ($\beta^E$), excess free length ($L_f^E$), and excess free volume ($V_f^E$), , all the parameters are positive in all the three systems over the entire range of composition [26]. suggests that the negative excess values has been due to closely packed molecules which account for the existence of strong interaction and positive excess values to weak interactions between unlike molecules due to dispersion forces. Further, the interactions between unlike molecules predominantly rupture the hydrogen-bonding structures, which is the main cause of excess compressibility. Further, an almost increasing trend of excess freelength either continuously or attaining maximum, indicates the presence of specific interactions between the different sizes of the molecules [27-29]. The values of excess free volume in all the three systems are positive which may be due to the weakening of dipolar interaction between the molecules of the mixtures. The negative excess internal pressure in all the systems clearly confirms this prediction.

## Conclusion

From the present investigation, it is obvious that there exists an interaction between DMF (proton acceptor) and 1-alkanols is due to hydrogen bonding, and further addition of DMF disassociates the associated structure of 1-alkanols. The rupture of H-bonded associates of alkanols dominates over that of H-bonding between unlike molecules. The DMF- alkanols interaction is weaker than DMF-DMF interaction and alkanol -alkanol interaction. It is eventually seen that a weak interaction is observed in the present study.

## References

[1] Madhu Rastogi; Aashees Awasthi; Manisha Gupta; J.P. Shukla; *Ind. J. Pure & Appli. Phys.*, **2002**, *40*, 256.
[2] S. Acharya; R. Paikray; G.C. Mohanty; *Ind. J. Pure & Appli. Phys*, **2003**, *41*, 855.
[3] S.L. Oswet; A.J. Patel; *J. Chem. Eng. Data*, **1995**, *40*, 194.
[4] Anwar Ali; Anilkumar; Abida; *J. Chinese Chem. Soci.*, **2004**, *51*, 477.
[5] J.S. Rowlison; *Liquid and Liquid mixtures*, 2nd Edn., Butter Worths, London, **1969**, 159.
[6] P. Venkatesu; R.S. Ramadevi; M.V. Prabakara Rao; *J. Pure & Appl. Ultrasonics*, **1996**, *18*, 16.
[7] Surjit Singh Bhatti; Devinder Pal Singh; *Ind. J. Pure & Appli Physics*, **1996,** *21*, 506.
[8] U. Srinivasalu; P. Ramachandra Naidu; *J. Pure & Appl. Ultrasonics*, **1995**, *17*, 14.
[9] J.D. Pandey; V.N. Srivatsava; V. Vimala; N. Panta; *Ind. J. Pure & Appli Physics*, **1987**, *25*, 467.
[10] R.D. Rai; R.K. Shukla; A.K. Shukla; J.D. Pandey; *J. Chem. Thermoidynamics*, **1989**, *21*, 125.
[11] AN. Kannappan; V. Rajendran; *Acustica*, **1991**, *75*, 192.
[12] J.D. Pandey; A.K. Shukla; T. Neelima; G.P. Dubey; *Pramana*, **1993**, *40*, 81.
[13] T.N. Sri Vatsava; R.P. Singh; *Acoust. Lett* **1983**, *6*, 152.
[14] K. Ramaswamy; AN. Kannappan; D. Anbanantham; *Acoustica*, (Germany). **1980**, *44*, 342.
[15] R. Mishra; J.D. Pandey; *J. Acoust. Soc. Ind.*, **1979,** *7*, 145.
[16] AN. Kannappan; V. Rajendran; *Ind. J. Pure & Appl. Phys.*, **1991**, *29*, 466.
[17] A. Ali; S. Hyder; A.K. Nain; *Ind. J. Phys*, **2000**, *74B(1)*, 63.
[18] A. Ali; S. Hyder, A.K. Nain; *Acoustt Lett.*, **1988**, *21*, 77.
[19] L. Palaniappan; Ph.D Thesis, Annamalai University, **1998**.
[20] P.L. Soni; A Text Book of Organic Chemistry, Sultan & Chand Sons Ltd., New Delhi, **1998**.
[21] Anwar Ali; Anil Kumar Nain; Dinesh Chand; Bhajan Lal; *Ind J. Pure & Appl. Phys.* **2003**, *41*, 928.
[22] A. John Dean; *Lange's Hand Book of Chemistry*, Mcgraw Hill International 13th edition, New York, **1987**.
[23] D. Anbananthan; *J. Acoust, Soc, India.*, **1979**, *7*, 123.
[24] V. Rajendiran; *Ind. J. Pure & Appl Phys*, **1994**, 32, 523.

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[25] AN. Kannappan; V. Rajendran; K. Ramalingam; R. Palani; *Ind. J. Phys.* **1991,** *65B(3)*, 266.
[26] U. Sri Devi; K. Samatha; A. Visvanatasarma; *Ind J. Pure & Appl. Ultrasonics,* **2004,** *26*, 1.
[27] K.C. Reddy; S.V. Subramanyam; Bhimsenachar; *J.Phys Soc. Jap,* **1964**, *19*, 559.
[28] C.V. Chaturvedi; S. Prakash; *Acoustica*, **1972**, *27*, 248.
[29] S.C. Agnihotri; J. Prakash Om; *Acoust. Soc. Ind.*, **1985**, *13*, 182.