

Study of molecular interactions and ultrasonic velocity in mixtures of some alkanols with aqueous propylene glycol

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Ultrasonic velocity, density and viscosity are experimentally determined in the mixtures of methanol/ethanol with aqueous propylene glycol (4.5m and 1.5m) over entire range of composition at 303.15K. Several acoustic and thermodynamic parameters such as excess viscosity, excess adiabatic compressibility, excess free volume, excess molar volume, excess enthalpy, excess free length, viscous relaxation time have been calculated to study nature and extent of molecular interactions in these mixtures. Ultrasonic velocities theoretically evaluated using Nomoto's relation, Van Dael and Vangeel's ideal mixing relation, impedance relation, Jacobson's equation, Rao's specific sound velocity relation and Junjie's equation are compared with experimental values to check applicability of these equations to the systems studied. The departure of experimental values of ultrasonic velocities from theoretical values is further analyzed to investigate molecular interactions. Two types of polynomial equations are fitted to experimental values of ultrasonic velocities. These polynomial representations of sound velocities have extremely small deviations from experimental values.

Keywords: Ultrasonic velocity, Molecular interactions, Liquid mixtures, Aqueous propylene glycol, Alkanols

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1 Introduction

The properties of liquid mixtures and solutions can be altered continuously within a reasonable range by varying the concentration till an optimum value of some desired parameter is attained. The pure liquids lack such flexibility. The study of properties of liquid mixtures and solutions finds direct applications in chemical and biochemical industry¹⁻³. Speed of sound, itself, is highly sensitive to the structure and interactions present in the liquid systems as it is fundamentally related to the binding forces between the constituents of the medium⁴. The measurement of speed of sound in liquids enables determination of some useful acoustic and thermodynamic parameters that are found to be very sensitive to molecular interactions. Hence, such measurements are useful to study the strength of molecular interactions in liquid mixtures.

Water and alcohol mixtures show unique maxima and minima in their thermodynamic and acoustic properties at low alcohol concentrations^{5,6}. The formation of such maxima/minima in aqueous solutions of electrolytes⁷ and in non-aqueous solutions⁸ is also reported in literature. The study of propylene glycol is important due to its wide range of applications in medicine and industry. It is used as (1) moisturizer in medicines, cosmetics, food and tobacco

products (2) medical lubricant (3) solvent for food colours and flavourings (4) main ingredient in cosmetic products (5) in smoke machines to make artificial smoke and (6) in antibacterial lotions and saline solutions. The ultrasonic study of molecular interactions in the mixtures of aqueous propylene glycol and some alkanols (methanol and ethanol) has been reported in this paper.

2 Experimental Details

The ultrasonic velocity is measured using a variable path ultrasonic interferometer working at 2MHz with an accuracy of ± 1 part in 10^4 . In this method, the wavelength of ultrasonic wave is accurately determined at the working frequency. The temperature of the interferometer cell is maintained by circulating water pumped from a constant temperature water bath, around the cell.

The density is measured using a two-stem pycnometer. In this method, the calibration of volume of pycnometer is done using triply distilled water, as it is not practicable to determine the volume of pycnometer cell exactly from its geometry. The capillary of the pycnometer is calibrated using mercury and the estimated accuracy in this method is 1 in 10^5 parts.

The viscosity is determined using Ostwald viscometer, which is calibrated at all the temperatures investigated using triply distilled water. In this method, the time of flow of a given volume of sample liquid, through a capillary is compared with that of a reference liquid of known density and viscosity. The viscosity of sample liquid can be determined if the density of the sample liquid is known. The estimated accuracy in the measurement of viscosity is $\pm 0.1\%$. The measurement of ultrasonic velocity, density and viscosity is made at 303.15K.

The solutions of aqueous propylene glycol at 4.5m and 1.5m are prepared using triply distilled water. These solutions in turn are used to prepare liquid mixtures with methanol and ethanol so that entire range of composition is covered (i.e. 0 to 100% alkanol).

3 Theory

Using experimentally measured values of ultrasonic velocity (u), density (ρ) and viscosity (η), the following acoustic and thermodynamic parameters are evaluated.

- 1 Adiabatic compressibility : $\beta = 1/(u^2\rho)$
- 2 Free volume : $V_f = (M_{eff}u/K\eta)^{3/2}$
- 3 Internal pressure : $\Pi_i = bRT (K\eta/u)^{1/2}(\rho^{2/3}/M_{eff}^{7/6})$
- 4 Molar volume : $V_m = M_{eff}/\rho$
- 5 Enthalpy : $H = \Pi_i V_m$
- 6 Viscous relaxation time : $\tau = 4\eta/(3\rho u^2)$
- 7 Free length : $L_f = K_j\beta^{1/2}$

where $K = 4.28 \times 10^9$; K_j is the Jacobson's constant which is temperature dependant; b the packing factor and its value for cubic packing is 2; T the absolute temperature; R the universal gas constant and M_{eff} is the effective molecular weight of the solution.

Excess values of various acoustic and thermodynamic parameters are calculated using the relation $Y^E = Y_{exp} - Y_{ideal}$, where Y^E is the excess value of the parameter Y , Y_{exp} is the experimental value of the parameter Y , $Y_{ideal} = x_1Y_1 + x_2Y_2$; x_1, x_2 are the molefractions and Y_1, Y_2 are the values of the parameter Y in the component liquids of the liquid mixture. In the above calculations, solution of aqueous propylene glycol is considered as one component of the mixtures.

4 Results and Discussion

The variation of ultrasound velocity with molefraction of methanol and ethanol is presented in Figs 1 and 2 which is monotonic in case of liquid

mixtures of methanol and 4.5m aqueous propylene glycol. But the velocity of sound shows a clear maximum at about 0.1m molefraction of methanol with 1.5m aqueous propylene glycol. The ultrasonic velocity graph shows a clear peak at about 0.1 m molefraction of ethanol with both 1.5 m and 4.5 m aqueous solutions of propylene glycol solutions.

Water and propylene glycol are both associated liquids, associated through hydrogen bonding. Association between propylene glycol and water molecules takes place through hydrogen bonding when propylene glycol is added to water. This leads to the increase of open structures in the solution as diol acts as a structure maker.

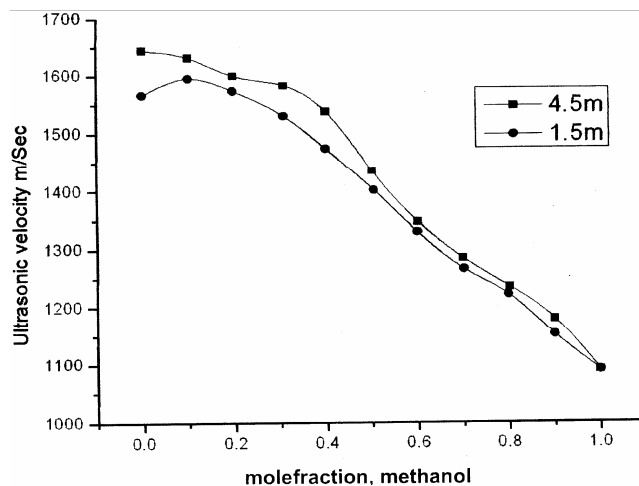


Fig. 1 — Variation of ultrasonic velocity in the mixtures of methanol and aqueous propylene glycol

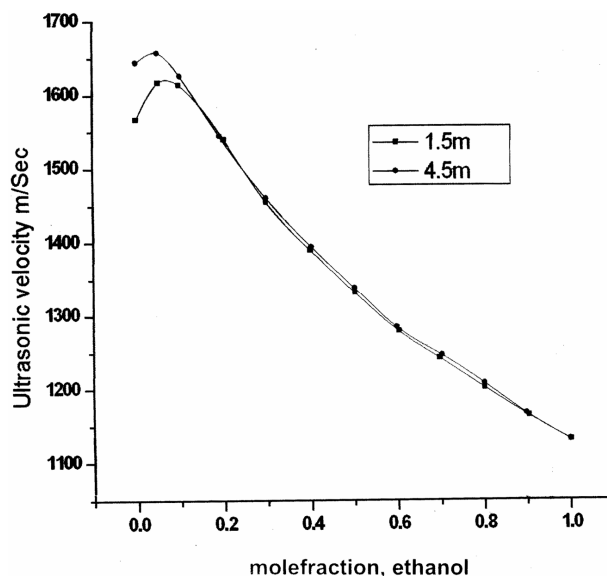


Fig. 2 — Variation of ultrasonic velocity in the mixtures of ethanol and aqueous propylene glycol

The conclusions are evident from the observations that (1) velocity and density of 1.5 m and 4.5 m aqueous solutions of propylene glycol are higher than the corresponding values of the pure components i.e. water and propylene glycol (2) adiabatic compressibility of 1.5 m and 4.5 m aqueous propylene glycol solutions are lower than the corresponding values of pure components.

In the mixtures of alkanols and aqueous propylene glycol, velocity maximum is observed in the low concentration region of alkanol. The origin of maximum in the low concentration region of alkanol is due to long-range order in water giving rise to hydrogen bonded structure⁵. Such a structure has many cavities and these cavities can accommodate solute molecules (in this case *n*-alkanol molecules). This is further favoured by the large difference in molar volume between the components of the solution. As alkanol is added to the aqueous propylene glycol, alkanol molecules go on occupying the cavities in the water molecular aggregates (open structures) and water + propylene glycol structures. This gives rise to a denser packing of molecules resulting in increase of ultrasonic velocity of solutions. This process continues till all cavities are filled. Thereafter, adding alkanol to aqueous propylene glycol molecules increases unassociated monomer structures in the solution. There is also some possibility for *n*-alkanol molecules disrupting the hydrogen bonding between the water-propylene glycol molecules resulting in unassociated propylene glycol molecules in the solution. Thus, the structure of solution becomes more and more loosely packed by increasing the concentration of alkanol molecules. As such ultrasound velocity in the solution decreases. Hence, the intermolecular complex formation is taking place in the low alkanol concentration region of the solution.

In case of mixtures of methanol and 4.5 m aqueous propylene glycol, the variation of ultrasound velocity suggests that by adding methanol to aqueous propylene glycol the structure of solution is becoming more and more loosely packed. This in turn indicates that addition of methanol to 4.5m aqueous propylene glycol, molecular interactions resulting in disruption of open structures and water+propylene glycol aggregates dominate other structure making tendencies.

The variation of viscosity in the mixtures of alkanols and aqueous propylene glycol is presented in Figs 3 and 4. The viscosity of the systems rises with

increasing concentration of alkanol and attains a maximum. There afterwards viscosity decreases with increase in concentration of alkanol. Several instances of such maxima are reported in literature^{9,10}. Generally, the viscosity of a system decreases with increasing number of smaller entities and decreasing number of bulk or less mobile entities in the system¹¹. Viscosity increases with decreasing number of small entities and increasing number of bulk entities or less mobile entities. Non-monotonic variation of viscosity is explained in water + amide solutions on the basis of complex formation by Assarson and Eirich¹² and in dimethylsulphoxide and TCE binary mixtures by Ali and Soghra¹. Well-defined peak in viscosity is an indication of strong interactions involving dipole-dipole associations, acceptor-donor type interactions

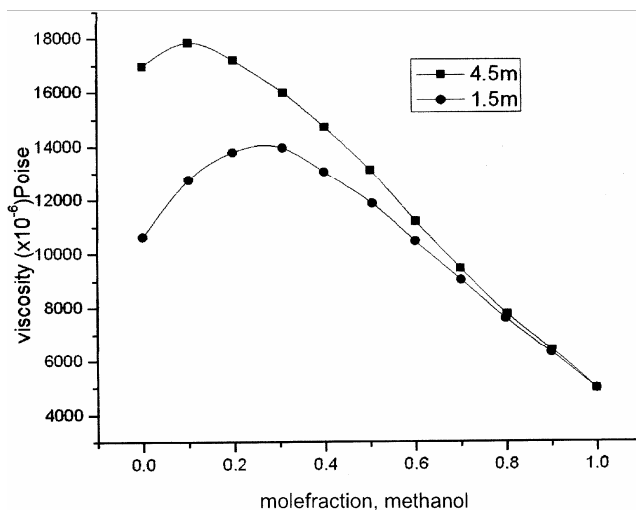


Fig. 3 — Variation of viscosity in the mixtures of methanol and aqueous propylene glycol

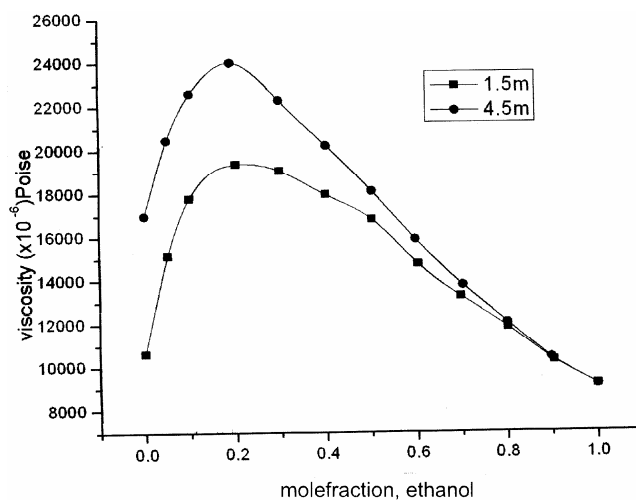


Fig. 4 — Variation of viscosity in the mixtures of ethanol and aqueous propylene glycol

and other interactions that favour complex formation between component molecules. It is well known that alcohol molecules are highly polar and in addition they can accept as well donate protons. Hence, the dipole-dipole and acceptor-donor type interactions are also possible in addition to the already explained hydrogen bonding interaction.

The viscosity of the systems is decreasing with increase of alkanol concentration in the alkanol rich region. This may primarily be due to the domination of dissociation of hydrogen bonded clusters present in the solution over associative interaction operating between the component molecules.

The deviation of a physical property of the liquid mixture from the ideal behaviour is a measure of the interaction between molecules, which is attributed to either adhesive or cohesive forces. Thus, the study of excess parameters plays an important role to study the molecular interactions. The variation of excess viscosity is presented in Figs 5 and 6. The excess viscosity is positive over the entire composition range. The negative values of excess viscosity indicate that dispersive forces arising from weak molecular interactions are operative in the system. The positive values of excess viscosity suggest that specific interactions are prevalent in the system^{12,13}. The variation of excess viscosity in the present case suggests that specific interactions such as formation of new hydrogen bonds, formation of charge transfer complexes, dipole-dipole interactions and other complex forming interactions are dominant in the systems investigated as the alcohols are highly polar and water is also polar.

The variation of excess adiabatic compressibility, excess molar volume and excess free volume is

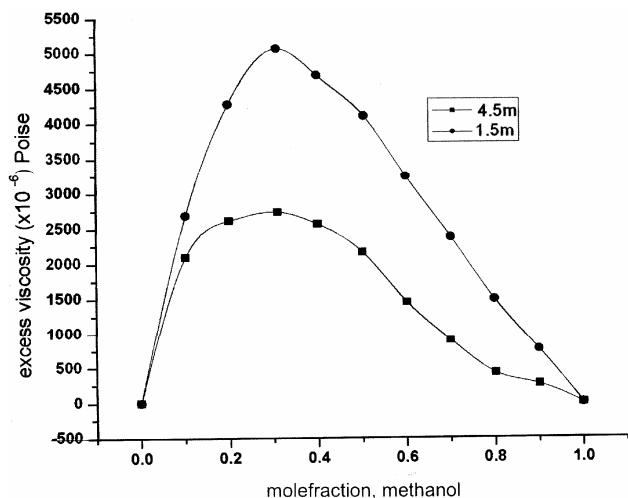


Fig. 5 — Variation of excess viscosity in the mixtures of methanol and aqueous propylene glycol

presented in Figs 7-12. The adiabatic compressibility is a measure of ease with which the system can be compressed. The excess adiabatic compressibility is negative over the entire composition range of mixtures investigated in the present study. The negative values of excess adiabatic compressibility indicate that the liquid mixture is less compressible than the pure liquids forming the solution and molecules in the mixture are more tightly bound in the liquid mixture than in pure liquids. Thus, negative values of excess adiabatic compressibility indicate strong specific interactions between component molecules and interstitial accommodation of smaller molecules in the voids created by bigger molecules. The excess molar volume and the excess free volume

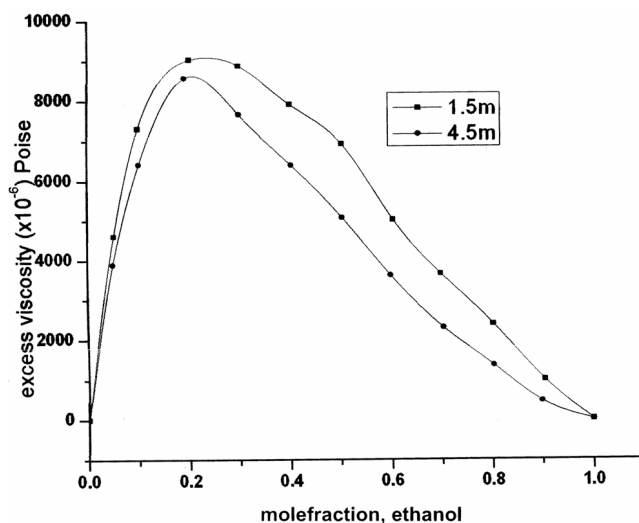


Fig. 6 — Variation of excess viscosity in the mixtures of ethanol and aqueous propylene glycol

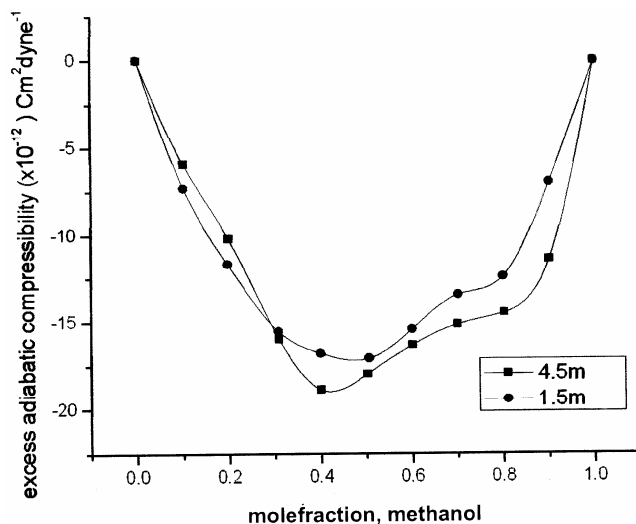


Fig. 7 — Variation of excess adiabatic compressibility in the mixtures of methanol aqueous propylene glycol

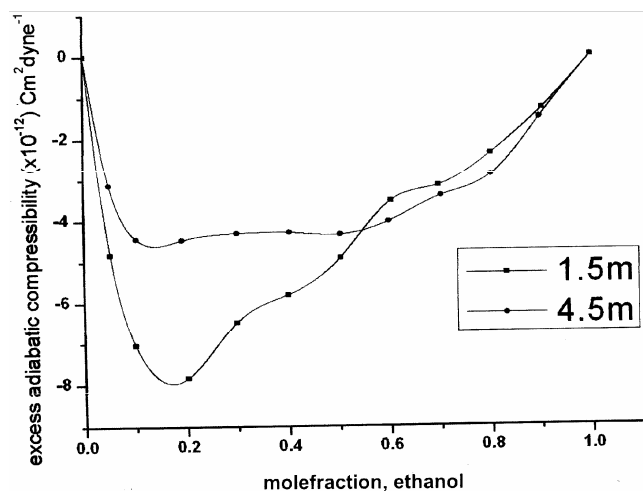


Fig. 8 — Variation of excess adiabatic compressibility in the mixtures of ethanol aqueous propylene glycol

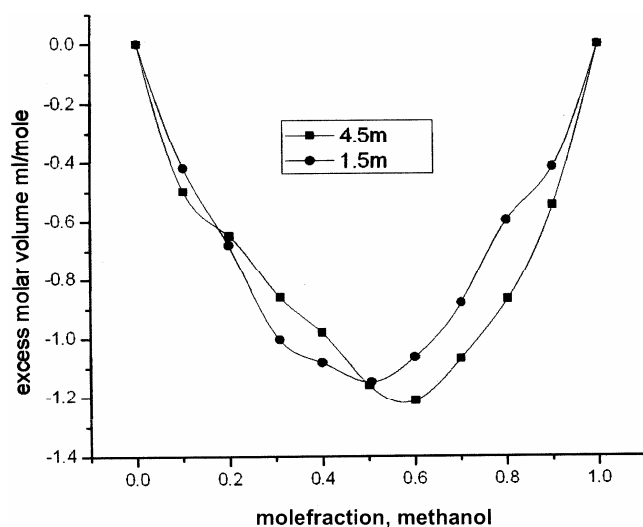


Fig. 9 — Variation of excess molar volume in the mixtures of methanol and aqueous propylene glycol

are negative over the entire composition range of mixtures. This suggests that the component molecules are more close together in the liquid mixture than in the pure liquids forming the mixture, indicating that strong attractive interactions between component molecules such as hydrogen bonding, dipole-dipole interactions and other specific interactions between unlike molecules are operative in the system. The marked difference between molar volume (roughly more than two times) between the aqueous propylene glycol and alkanols favours fitting of component molecules into each others structures, thereby reducing volume of mixtures resulting in negative excess adiabatic compressibility, negative molar volume and negative free volume^{13,14}.

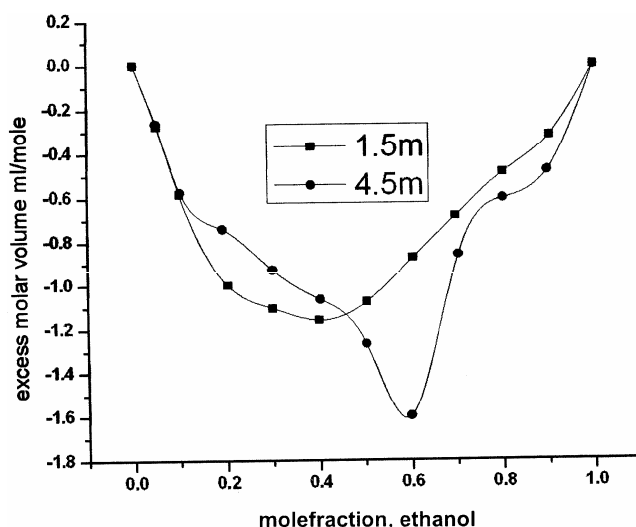


Fig. 10 — Variation of excess molar volume in the mixtures of ethanol and aqueous propylene glycol

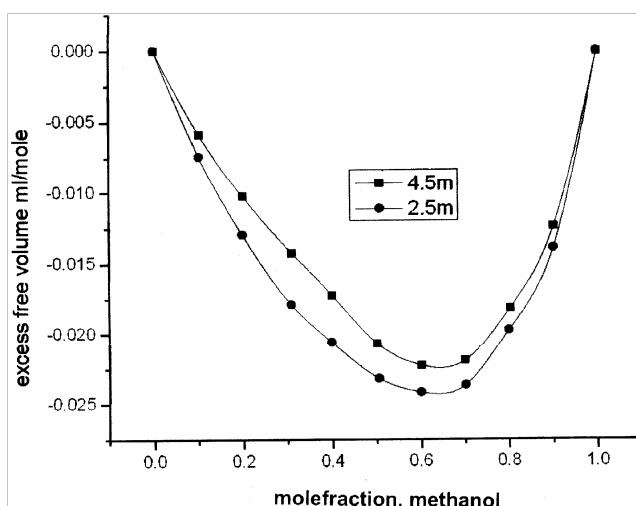


Fig. 11 — Variation of excess free volume in the mixtures of methanol and aqueous propylene glycol

The variation of excess free length is presented in Figs 13 and 14. The excess free length is negative over the entire range of composition investigated exhibiting a minimum. This indicates structural readjustment in the liquid mixtures towards a less compressible phase of fluid and closer packing of molecules^{8,15}. This aspect further supports the variation of other excess parameters.

The variation of excess enthalpy is presented in the Figs 15 and 16. The excess enthalpy is positive over entire composition range studied. The positive values of excess enthalpy suggest strong bonding and exothermic reactions. Thus, it can be concluded that strong specific interactions are operative in the systems investigated. The concentration of mixture

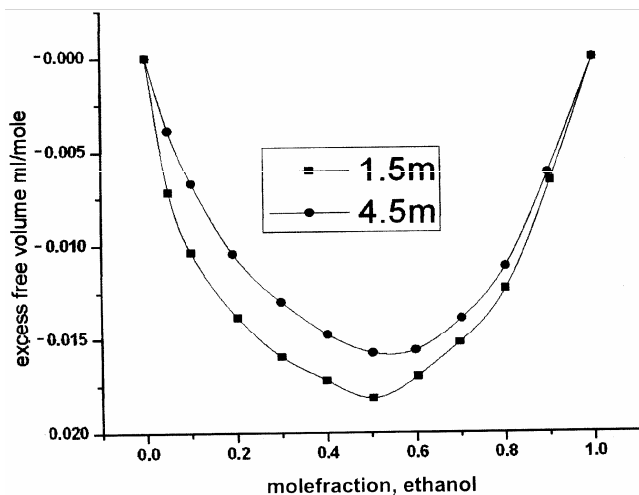


Fig. 12 — Variation of excess free volume in the mixtures of ethanol and aqueous propylene glycol

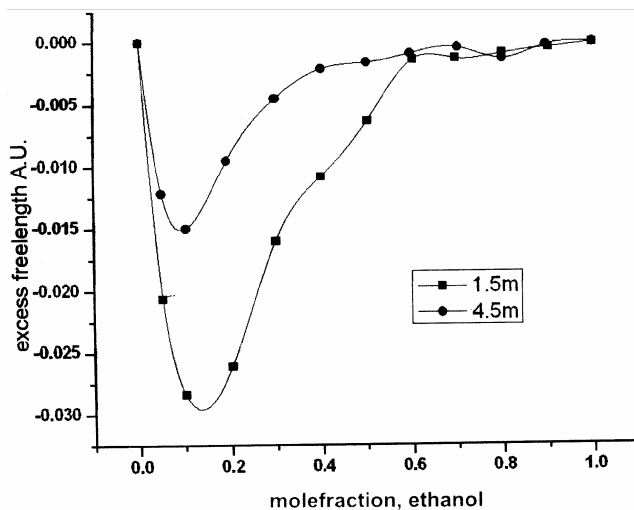


Fig. 14 — Variation of excess free length in the mixtures of ethanol and aqueous propylene glycol

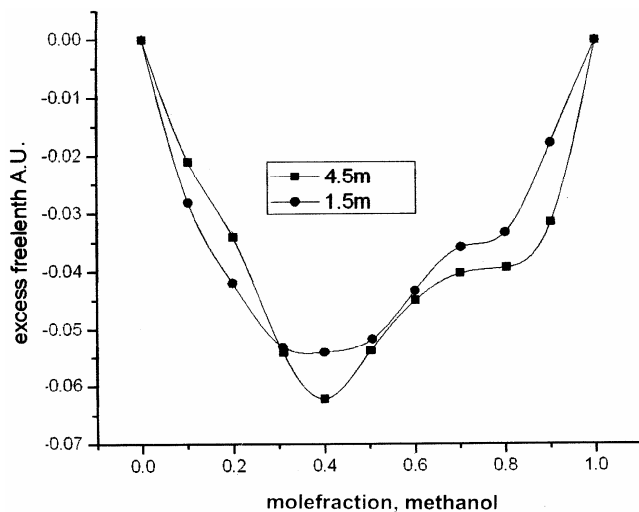


Fig. 13 — Variation of excess free length in the mixtures of methanol and aqueous propylene glycol

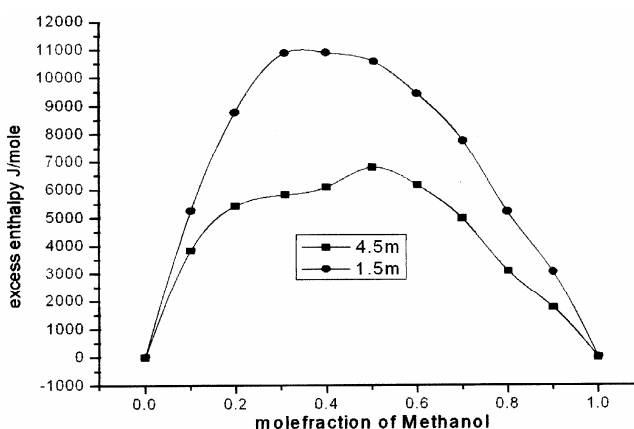


Fig. 15 — Variation of excess enthalpy in the mixtures of methanol and aqueous propylene glycol

corresponding to velocity maximum in the systems investigated is less than the concentration corresponding to excess enthalpy maximum. This indicates that stoichiometry corresponding to complex formation does not correspond to the most stable configuration of molecules in the mixtures investigated.

The variation of viscous relaxation time is non-linear and non-monotonic and is presented in Tables 1 and 2. The viscous relaxation time increased with increase in alkanol concentration and attained a maximum value. Further, increasing alkanol concentration resulted in decrease of viscous relaxation time. This variation supports the above discussion that molecular complex formation is taking

place due to strong specific interactions operative in the system.

The variation of excess viscosity gives a qualitative estimation of the strength of molecular interactions. According to Fort and Moore¹⁶, excess viscosity becomes more positive as the strength of interaction increases. The variation of excess viscosity in the present study clearly indicates that strength of interactions in the mixtures of alkanols is more with 1.5 m aqueous propylene glycol than with 4.5 m aqueous propylene glycol. The conclusion is supported by the observation found in the variation of ultrasonic velocity with concentration of methanol. In the mixtures of methanol and 4.5 m aqueous propylene glycol, interactions are not strong enough to produce a maximum in the velocity versus concentration curve. But a velocity maximum is

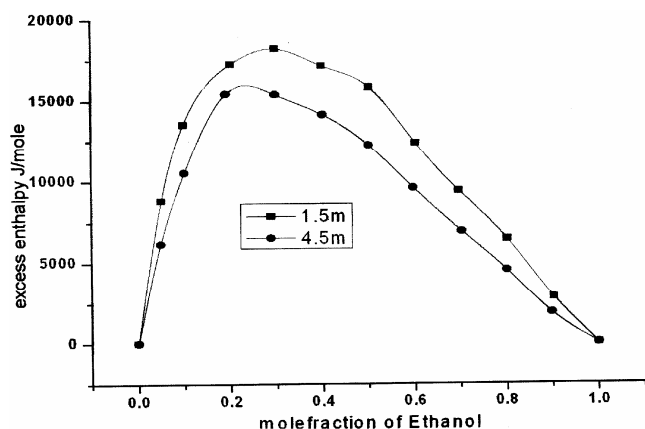


Fig. 16 — Variation of excess enthalpy in the mixtures of ethanol and aqueous propylene glycol

Table 1 — Variation of viscous relaxation time in the mixtures of methanol and aqueous propylene glycol

1.5 m aqueous propylene glycol		4.5 m aqueous propylene glycol	
Molefraction	Viscous relaxation time ($\times 10^{-12}$) sec	Molefraction	Viscous relaxation time ($\times 10^{-12}$) sec
0.0000	5.79	0.0000	8.29
0.1009	6.85	0.1013	9.02
0.1979	7.80	0.1988	9.31
0.3084	8.55	0.3092	9.10
0.3993	8.84	0.4002	9.08
0.5054	9.12	0.5012	9.50
0.6001	9.17	0.6011	9.43
0.7012	8.96	0.6996	9.01
0.7994	8.31	0.8021	8.21
0.9001	7.91	0.9009	7.65
1.0000	7.14	1.0000	7.14

Table 2 — Variation of viscous relaxation time in the mixtures of ethanol and aqueous propylene glycol

1.5m aqueous propylene glycol		4.5m aqueous propylene glycol	
Molefraction	Viscous relaxation time ($\times 10^{-12}$) sec	Molefraction	Viscous relaxation time ($\times 10^{-12}$) sec
0.0000	5.79	0.0000	8.29
0.0512	7.89	0.0497	10.01
0.0996	9.42	0.1016	11.64
0.2018	11.62	0.1916	14.22
0.2980	13.24	0.1989	15.26
0.3993	14.07	0.4020	15.62
0.5026	14.75	0.5021	15.52
0.6031	14.40	0.5982	14.99
0.6976	13.98	0.7024	14.30
0.8014	13.57	0.8011	13.61
0.9027	12.76	0.8978	12.78
1.0000	12.20	1.0000	12.20

observed in case of mixtures of methanol and 1.5 m aqueous propylene glycol.

The experimental values of sound velocities in liquid mixtures investigated and velocities calculated using various theories¹⁷⁻²² along with percentage errors in theoretical values from experimental values are summarized in Tables 3-6. Various theoretical formulae used for evaluating sound velocity are detailed hereafter. Such an evaluation offers a simple method to investigate molecular interactions besides verifying the applicability of various theories to liquid mixtures. In the present study, theoretical velocities are evaluated by considering aqueous propylene glycol as one component in the binary liquid mixture.

On assuming additivity of molar sound velocity Nomoto established the following equation for sound velocity:

$$U_N = \{(\sum x_i R_i) / (\sum x_i V_i)\}^3$$

where x_i is the molefraction, $R_i = u_i V_i^{1/3}$ the molar sound velocity, V_i the molar volume and u_i is the sound velocity of the i^{th} component.

Van Dael and Vangeel obtained the relation:

$$\Sigma(x_i/M_i u_i^2) = \{1/\Sigma x_i M_i\} \{1/U_V\}^2$$

where M_i is the molecular weight of i^{th} component in the liquid mixture.

Jacobson's equation is given by:

$$U_J = K\rho^{-1/2} L_f^{-1}$$

where L_f is the ideal free length of the mixture.

Impedance relation is given by:

$$U_{im} = \Sigma x_i Z_i / \Sigma x_i \rho_i$$

where Z_i is the acoustic impedance and ρ_i is the density of the i^{th} component of the mixture.

Rao's (specific sound velocity) relation is given by:

$$U_R = (\Sigma x_i r_i \rho)^3$$

where $r_i = u_i^{1/3} / \rho_i$ is the Rao's specific sound velocity of the i^{th} component of the mixture.

Junjie's equation is given by :

$$U_{Jun} = \{\Sigma x_i V_i / (\Sigma x_i M_i)^{1/2}\} \{\Sigma(x_i V_i / \rho_i u_i^2)\}^{-1/2}$$

Table 5A — Experimental and theoretical values of ultrasonic velocity in the mixtures of ethanol and 1.5 m aqueous propylene glycol m/S

Molefraction	U_{exp}	U_N	U_{imp}	U_J	U_R	U_V	U_{Jun}	$f(x)$	$g(x)$
0.0000	1567.0	1567.0	1567.0	1567.0	1567.0	1567.0	1567.0	1567.8	1567.9
0.0512	1617.2	1500.1	1549.4	1536.7	1517.3	1522.5	1450.4	1615.8	1616.1
0.0996	1614.1	1448.9	1532.3	1506.5	1490.0	1484.5	1379.6	1613.8	1614.2
0.2018	1540.1	1366.6	1495.1	1450.7	1418.5	1415.0	1289.6	1541.2	1540.8
0.2980	1455.2	1310.4	1458.4	1405.8	1340.0	1360.3	1240.7	1457.4	1457.5
0.3993	1390.0	1265.5	1418.0	1359.6	1281.3	1311.4	1207.3	1386.1	1386.6
0.5026	1331.9	1229.9	1374.7	1315.8	1230.5	1268.7	1183.9	1330.6	1330.5
0.6031	1279.1	1202.1	1330.4	1275.9	1188.7	1233.0	1167.3	1283.5	1283.0
0.6976	1242.2	1180.6	1286.6	1239.2	1163.0	1203.6	1155.5	1240.8	1240.9
0.8014	1202.0	1160.8	1236.0	1200.2	1146.5	1175.4	1145.2	1198.9	1199.5
0.9027	1164.1	1144.5	1183.9	1163.3	1140.3	1151.3	1137.3	1166.4	1165.9
1.0000	1131.0	1131.0	1131.0	1131.0	1131.0	1131.0	1131.0	1130.3	1130.3

Table 5B — Percentage deviation of theoretical velocities from experimental velocities

Molefraction	% ΔU_N	% ΔU_{imp}	% ΔU_J	% ΔU_R	% ΔU_V	% ΔU_{Jun}	% $\Delta f(x)$	% $\Delta g(x)$
0.0000	0.00	0.00	0.00	0.00	0.00	0.00	-0.05	-0.06
0.0512	7.24	4.19	4.97	6.18	5.86	10.32	0.08	0.07
0.0996	10.24	5.07	6.67	7.63	8.03	14.53	0.02	-0.01
0.2018	11.27	2.92	5.80	7.89	8.12	16.27	-0.07	-0.05
0.2980	9.95	-0.22	3.40	7.92	6.52	14.74	-0.15	-0.16
0.3993	8.95	-2.01	2.19	7.82	5.66	13.14	0.28	0.25
0.5026	7.66	-3.21	1.21	7.61	4.74	11.11	0.10	0.11
0.6031	6.2	-4.01	0.25	7.07	3.61	8.74	-0.34	-0.30
0.6976	4.96	-3.57	0.24	6.38	3.10	6.98	0.11	0.10
0.8014	3.43	-2.83	0.15	4.62	2.21	4.72	0.26	0.21
0.9027	1.69	-1.70	0.07	2.05	1.10	2.31	-0.20	-0.16
1.0000	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.04

It can be observed from Tables 3-6 that the deviation of theoretical values of sound velocities from experimental values is marked in the region where alkanol concentration is low. This implies that non-ideal behaviour of the system is predominant in this region, suggesting that strong specific interactions are operative in this low alkanol concentration region²³.

Nomoto's relation is based on additivity of molar sound velocity and isochoric condition under which volume remains unchanged even after mixing of the components. But large positive deviations of experimental values from the theoretical values computed using Nomoto's relation imply that molar sound velocity is not additive and volume of the system does not remain constant. This is probably due to complex formation already described and strong specific interactions. The large positive deviations of experimental values from theoretical values calculated

using Van Dael and Vangeel equation might be due to large negative deviation of adiabatic compressibility from the rectilinear dependence on the compressibility of the component liquids in the mixtures. This implies that chemical forces such as hydrogen bonding, dipole-dipole interactions between unlike molecules are present in the system. The large positive deviations of experimental values from values calculated using impedance relation and Rao's relation imply non-additivity of acoustic impedance and Rao's specific sound velocity in the liquid mixtures. This is a bare consequence of existence of strong specific molecular interactions. Large positive deviation of experimental values from the values computed using Jacobson's equation implies that intermolecular free length in the liquid mixtures is less than the ideal free length. This indicates that component molecules in the liquid mixture have a more compact arrangement than in component liquids

Table 6A — Experimental and theoretical values of ultrasonic velocity in the mixtures of ethanol and 4.5 m aqueous propylene glycol m/S

Molefraction	U_{exp}	U_N	U_{imp}	U_J	U_R	U_V	U_{Jun}	$f(x)$	$g(x)$
0.0000	1644.1	1644.1	1644.1	1644.1	1644.1	1644.1	1644.1	1646.8	1646.8
0.0497	1657.6	1574.2	1624.2	1606.2	1594.2	1601.4	1514.0	1652.1	1651.9
0.1016	1626.2	1513.6	1602.9	1566.4	1559.8	1560.1	1426.0	1626.5	1626.3
0.1916	1544.9	1430.0	1564.8	1510.6	1458.8	1495.2	1330.9	1550.8	1550.7
0.2989	1460.7	1355.0	1517.1	1446.4	1376.4	1427.2	1264.0	1458.9	1459.5
0.4020	1394.6	1299.9	1468.9	1388.5	1319.8	1369.6	1223.2	1389.5	1389.8
0.5021	1338.3	1257.4	1419.6	1334.0	1290.1	1319.7	1195.8	1336.4	1335.9
0.5982	1285.0	1224.0	1369.9	1282.7	1285.1	1276.3	1176.3	1291.0	1290.5
0.7024	1246.4	1193.8	1312.9	1245.5	1199.1	1233.6	1160.3	1244.1	1244.5
0.8011	1208.1	1169.8	1256.0	1205.4	1169.5	1196.7	1148.4	1203.9	1204.7
0.8978	1166.9	1149.5	1197.0	1166.5	1157.5	1163.5	1139.1	1170.6	1169.9
1.0000	1131.0	1131.0	1131.0	1131.0	1131.0	1131.0	1131.0	1130.2	1130.5

Table 6B — Percentage deviation of theoretical velocities from experimental velocities

Molefraction	% ΔU_N	% ΔU_{imp}	% ΔU_J	% ΔU_R	% ΔU_V	% ΔU_{Jun}	% $\Delta f(x)$	% $\Delta g(x)$
0.0000	0.00	0.00	0.00	0.00	0.00	0.00	-0.16	-0.16
0.0497	5.03	2.01	3.10	3.83	3.39	8.66	0.33	0.34
0.1016	6.93	1.43	3.68	4.08	4.07	12.31	-0.02	0.00
0.1916	7.44	-1.29	2.22	5.57	3.22	13.85	-0.38	-0.37
0.2989	7.23	-3.89	0.98	5.77	2.29	13.47	0.12	0.08
0.4020	6.79	-5.33	0.44	5.37	1.79	12.29	0.37	0.35
0.5021	6.04	-6.08	0.32	3.60	1.39	10.65	0.14	0.18
0.5982	4.75	-6.60	0.18	0.00	0.68	8.46	-0.47	-0.43
0.7024	4.22	-5.34	0.07	3.80	1.03	6.91	0.19	0.15
0.8011	3.17	-3.96	0.22	3.19	0.94	4.94	0.35	0.29
0.8978	1.49	-2.58	0.03	0.81	0.30	2.38	-0.32	-0.26
1.0000	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.05

Table 7 — Standard deviation of sound velocities calculated using polynomial equations from experimental values

Name of the liquid system	Polynomial form	Standard deviation m/S
Mixtures of methanol and 1.5 m aqueous propylene glycol	$f(x)$	3.73
	$g(x)$	3.78
Mixtures of methanol and 4.5 m aqueous propylene glycol	$f(x)$	7.52
	$g(x)$	7.26
Mixtures of ethanol and 1.5 m aqueous propylene glycol	$f(x)$	2.29
	$g(x)$	2.01
Mixtures of ethanol and 4.5 m aqueous propylene glycol	$f(x)$	3.87
	$g(x)$	3.62

forming the mixture. The velocity values computed using Junjie’s equation also confirm above predictions. The deviations in velocities decrease with increase in alkanol concentration in the alkanol rich region. This implies that specific interactions (between unlike molecules) are weakening with increasing alkanol concentration.

The authors tried to fit experimental velocity data to two types of polynomial equations described below, so that these empirical fittings qualitatively and quantitatively describe experimental velocity data even in the specific interaction predominant region where non-ideal behaviour of the system is marked. The polynomial equations attempted are:

$$f(x) = U(x) = \sum a_k x^k \text{ and}$$

$$g(x) = \ln U(x) = \sum (\ln U_k) x^k$$

where k in the summation assumes values from zero to six, x is the molefraction of the alkanol and a_k and $\ln U_k$ are constant coefficients to be determined using numerical methods. The values of sound velocities calculated, after determining the coefficients in the above equations by applying least squares method are presented in Tables 3-6.

The standard deviations corresponding to sound velocity values calculated using the polynomial equations from experimental values of sound velocities are evaluated using the relation:

$$\sigma = \{\Sigma(U_E - U_P)^2/n\}^{1/2}$$

where U_E is the experimental value of sound velocity, U_P the value of sound velocity calculated using the polynomial equations $f(x)$ and $g(x)$ and n is the number of samplings i.e. number of concentrations at which experimental or theoretical velocities are determined. The values of standard deviations are presented in Table 7. The standard deviations are very low and percentage errors presented in the Tables 3-6 are extremely small (related to these polynomial forms).

Equations of the type $g(x)$ have been attempted previously by some researchers³, where k in the summation assumes values from zero to four. But it is found, in the present study, that polynomial type fitting fails even to explain qualitative variation of sound velocity if k is limited to four.

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