



Volumetric and viscometric study of binary systems of alcohols with alkane at (298.15, 303.15, 308.15, 313.15 and 318.15) K and atmospheric pressure

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ABSTRACT

The excess molar volume V^E and viscosity coefficient of the binary mixtures of 1-propanol-, 2-methyl-2-propanol-, and 1-hexanol- with hexane over the whole composition range have been measured at five different temperatures (298.15, 303.15, 308.15, 313.15 and 318.15)K and atmospheric pressure. The observed values of the V^E for the mixtures can be explained in terms of the (i) dissociation of the associated polar molecules, (ii) dipole-induced dipole interaction between the polar and non-polar molecules, (iii) repulsive electronic force between the components and (iv) geometric effect due to differences in molar volumes. The V^E data have been fitted by the least square method to the five parameter Redlich-Kister equation and values of the parameter A_j have been reported. The excess viscosities η^E of all the mixtures are negative and have minima at around 0.40, 0.2 and 0.10 respectively mole fractions for x_1 of hexane. The values both η^E and interaction parameter d have been explained in the light of the observation of Nigam and Mahl. The free energies for viscous flow ΔG^z and the excess free energies for viscous flow ΔG^{zE} has been calculated from the equation of Eyring.

Keywords: Excess molar volume; Excess viscosity coefficient; Free energy for viscous flow

INTRODUCTION

The experimental approach of measurements of various macroscopic properties is also useful in providing guidance to theoretical approaches, since the experimentally determined values of solution properties may bring to light certain inadequacies in the proposed model on which theoretical treatments may be based. Thermodynamic studies on binary solutions have attracted a great deal of attention and experimental data on a good number of systems [1, 2]. There has also been considerable interest in the measurement of physicochemical properties [3,4] of particular interest has been the determination of viscosities of mixtures. The 1-alkanols are interesting simple examples of biologic and industrial important amphiphilic materials [5]. The effect of temperature and chain length of 1-alkanols when mixed with benzylalcohol that may induce changes in sign and magnitude of excess thermodynamic functions [6]. Further, it has been reported [7-9] that the strength of association in alkanols decreases as the carbon chain length in the molecule increases for 1-propanol, 1-butanol, 1-pentanol, and 1-hexanol. A survey of the literature has shown that the thermodynamic properties for binary liquid mixtures [10-18] were reported earlier. The knowledge of physicochemical properties of multicomponent mixtures was indispensable for many chemical process industries. For instance, in petroleum, petrochemical and related industries the above mentioned processes were commonly used to handle the mixture of hydrocarbons alcohols, aldehydes, ketones etc., which exhibit moderately ideal to highly non-ideal behavior. For accurate design of equipment required for these processes, it is necessary to have information regarding the interactions between the components. Similarly, knowledge of the viscosity of

liquids/mixtures is indispensable, since nearly all engineering calculations involve flow of fluids. Viscosity data yield a lot of information on the nature of intermolecular interaction and mass transport.

Some compilations [19] on the viscometric behaviour in liquid mixtures. Besides the objective of correlating the viscosity of mixtures with those of the pure components there has been a growing interest to determine certain criteria of fundamentals dependence of viscosity on thermodynamic properties. Interdependence of viscosity coefficients (which is a transport property) with thermodynamic properties is justifiable in view of the fact that their values depend on the characteristic distribution observed by the particles in any thermodynamic state. Although a very large number of equations have been proposed from time to time to express solution viscosity in terms of those of its components, none has really been proven to be of general applicability. Benson and co-workers [20] have reported very accurate data at 25°C for mixtures of alcohols and alkanes both throughout the whole range and at very dilute concentrations. They suggested that v^E is the resultant contributions from several apposing affects that may be divided in three types: chemical, physical and structural.

Shan and co-workers [21] determined the viscosities and densities of nine binary 1-alkanol systems of 1-propanol + 1-butanol, propanol + 1-pentanol, butanol + 1-pentanol, 1-butanol + 1-nonanol, 1-butanol + 1-decanol, 1-pentanol + 1-octanol, 1-heptanol + 1-octanol, 1-nonanol + 1-decanol, and 1-decanol + 1-undecanol over the entire composition range at 293.15 and 298.15K and atmospheric pressure. The experimental viscosity data were correlated by the McAllister three-body and four-body models and were used to test the predictive capability of the generalized corresponding state principle (GCSP) method.

Rambabu and co-workers [22] determined ultrasound velocities and densities of binary mixtures of 1-bromobutane with 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol and 1-octanol at 303.15K. Isentropic compressibilities (K_s) and deviations in isentropic compressibilities (ΔK_s) were calculated from the results. The values of ΔK_s were positive over the entire range of composition in all six binary liquid mixtures. The experimental results were explained in terms of depolymerization of H-bonded alcohol aggregates, decreases in dipolar association and weak hydrogen-bonding interaction of the type Br... H-O between unlike molecules. Aminabhavi *et al* [3] determined the densities, viscosities, and refractive indices of the binary mixture of bis(2-methoxyethyl)ether with 1-propanol, 1-butanol, 2-methyl-2-propanol. From these results, the excess molar volumes, deviations in viscosity and refractivity were calculated. The results were fitted to the Redlich-Kister polynomial equation and the binary interaction parameters were estimated.

Subha *et al* [23] measured densities and viscosities of propionic acid in methanol, ethanol, 1-propanol, 2-propanol and 1-butanol at 308.15K. From experimental data, the excess molar volumes, (V_M^E) excess viscosities, (η^E) and the excess molar Gibbs free energy for the activation of flow (G^{\ddagger}) were computed and presented as functions of composition. Rajendran [24] measured the ultrasonic velocity, density and viscosity for the binary liquid mixtures of n-heptane with n-propanol, iso-propanol, n-butanol and iso-butanol over the entire range of mole fractions at 298.15K. These data have been used for computing the molar volume, internal pressure and enthalpy of the mixtures. The positive contribution on V^E , H^E and negative contribution on Π_1^E , η^E indicates the absence of complex formation in the mixtures. Orge and his co-workers [25] presented experimental values of the density, refractive index, speed of sound, and dynamic viscosity of the binary mixtures (methanol, ethanol or 1-propanol) with (pentane, hexane, heptane and octane) at 298.15K and atmospheric pressure, as a function of the molar fraction. From the experimental values, the corresponding excess and deviation values were computed (excess molar volumes, change of refractive index on mixing, change of isentropic compressibilities and dynamic viscosity deviations), variable degree polynomials being fitted to the results. Different methods were applied in order to establish values of these physical properties, in good agreement with experiment. The binodal tie lines for each ethanol + alkane binary mixture at different temperatures were determined by the measurement of physical properties and application of the corresponding fitting polynomials. UNIFAC – Dortmund group contribution method was applied to predict these liquid – liquid equilibria.

Singh *et al* [26] measured the excess volumes for the binary mixtures of 1-propanol or 2-propanol + benzene, + toluene, + o-xylene, + m-xylene and + p-xylene over the entire range of composition at 298.15K. The excess volume curves for 1-propanol + toluene, + o-xylene and p-xylene systems were sigmoid. The observed V^E values of the mixture were positive over most of the concentration range, but slightly negative at $X_1 > 0.8$. The observed V^E

values of the system 2-propanol + benzene were positive over the entire range of composition. The results were discussed in terms of various physical, chemical and structural effects

The applicability of two molecular theories in predicting thermodynamic excess properties is tested. In particular the experimentally determined dependence of the excess enthalpy on pressure of some binary alkane + alkane and alcohol + alkane mixtures was used in this investigation. A consistent description of the experimental results of the alkane + alkane mixtures was possible using a modified Prigogine-Flory-Patterson free volume theory, which accounts for the short range order observed for n-alkanes. To the alcohol + alkane mixtures the real associated solution model has been applied in order to take into account the volume change upon mixing due to hydrogen bonding of the alcohols. This model, however, was found to be insufficient for describing quantitatively the pressure dependence of the excess enthalpy.

To our knowledge, the excess molar volumes, viscosities and free energies of five binary mixtures, viz., hexane + 1-propanol, + 2-propanol, + 2-methyl-2-propanol, + 1-hexanol, and + 1-heptanol at different temperatures and compositions have not been studied. This article reports the experimental density and viscosity data of the binary mixtures of the above compounds at (298.15, 303.15, 308.15, 313.15 and 318.15) K. From these data, the excess molar volumes and the viscosity deviations were first, to interpret the experimental results and suggest the structure of the solutions, and secondly, the applicability of the theory of viscosity suggested by Bloomfield and Dewan [27] for these mixtures.

MATERIALS AND METHODS

Hexane (Fluka chemika, GC > 95%), 1-propanol (Fluka chemika, GC > 98%), 2-methyl-2-propanol (Fluka chemika, purity > 99.7%), 1-hexanol (Fluka chemika, GC > 98%) were used without further purification. The purity of the chemicals was checked by comparing their densities and viscosities with literature values.

An electronic balance (Mettler Toledo, B204-S, Switzerland) with an accuracy of ± 0.0001 g was used for weighing. The densities of the pure liquid and liquid-liquid mixtures were measured using a high precision vibrating tube digital density meter (DMA 5000, Anton Paar, Austria) with a high precision in-built thermostat. The method is based on the principle of time-lapse measurement for certain number of oscillations of a vibrating U-shaped sample tube filled with the sample liquid. At constant temperature, the natural vibration period of the U-tube is related [33] to the density of liquid filling the tube. The design of the cell ensures identical volumes to be used for the measurement on different samples. Using a polyethylene syringe the sample was continuously and slowly injected from the upper port of the U-tube until the excess fluid flowed out of the lower part. This ensured that the inner surface of the cell was completely wet and there were no micro bubbles inside the U-tube. The syringe was kept as such in plugged. After the measurement, the sample was removed and air was passed, by built-in pump, through the tube to remove excess liquid. The tube was then rinsed several times with the solution of higher concentration and finally the solution was injected for the measurement. All the measurements were made starting from the lowest to the highest solute concentrations. The working of the density meter was checked by measuring the density of standard water sample supplied with the density meter.

The viscosity coefficients of the pure liquids and their mixtures under investigation were determined by a modified cannon-type viscometer. The inside wall of the viscometer was thoroughly cleaned with warm chromic acid so that there was no obstruction due to grease or any other impurity in the capillary and the liquid could freely move without leaving any drop behind. It was then rinsed thoroughly with distilled water, followed by rectified spirit and finally with acetone and was dried. The viscometer with the liquid was then clamped vertically in the water thermostat. The viscometer with the liquid inside was kept in the water thermostat for 15-20 minutes to obtain the working temperature maintained. The flow time of liquids was recorded by an electronic stopwatch reading up to 0.01 second. A constant temperature water thermostat was used for the measurements of density and viscosity of the liquids. The temperature of the thermostat was maintained constant to an accuracy of ± 0.01 K and read on a Beckman thermometer set at the working temperatures. The controlling device consisted of a toluene regulator, an immersion heater, two tungsten filament bulbs (60w and 200w), a transistorized electronic relay and a variable transformer. An efficient stirrer was used to ensure the constancy of temperature of water throughout thermostatic bath. A clean dust free rubber tube with a syringe pipette was attached to the smaller arm of the viscometer in order to suck the liquid/solution up to the upper bulb. On sucking the liquid/solution above the upper mark of the viscometer tube, it was released. For each solution, the efflux time was measured at least three times and the average

of the efflux times agreeing within ± 0.05 seconds was taken.

The viscometric constants A and B of the viscometers was evaluated at experimental temperatures (298.15, 303.15, 308.15, 313.15 and 318.15)K using spectroscopy grade of cyclohexane and heptane. The values of A and B for the viscometers used were given in Table-1.

3. Results and discussion

3.1 Discussions of excess molar volumes, V^E

The excess molar volumes V^E of the binary mixtures of hexane + 1-propanol, + 2-methyl-2-propanol, and + 1-hexanol have been determined at five different temperatures, viz., 298.15, 303.15, 308.15, 313.15 and 318.15K over the entire range of composition. The experimental values of V^E have been fitted by the least square method to the five parameter Redlich-Kister equation of the type,

$$V^E/cm^3 \text{ mole}^{-1} = x_1(1-x_1) \sum_{j=0}^4 A_j(2x_1-1)^j \quad (1)$$

The values of the coefficient A_j , and the standard deviation S, have been reported with the table 2. The plots of the V^E values against the mole fraction x_1 of hexane at all the temperatures have been shown in the Figures 1(a), (b) and (c) respectively. The V^E Vs. x_1 plots of all the five mixtures at 298.15 K have also been shown in Figure 2 for comparison.

3.2 Excess molar volumes and structure of the solution

The excess molar volume of the binary mixtures of hexane + 1-propanol, + 2-methyl-2-propanol, and + 1-hexanol have been determined at five different temperatures, viz., 298.15, 303.15, 308.15, 313.15 and 318.15K over the entire range of mole fractions. In Fig. 1(a) the V^E values for the hexane + 1-propanol mixtures were sigmoid, which were negative over the almost entire range of mole fractions (x_1) of hexane and small positive at higher x_1 values. In Fig. 1(b) and Fig. 1(c) shows the V^E values for the hexane + 2-methyl-2-propanol and + 1-hexanol were positive over the entire range of composition. The magnitudes of V^E values were in the order, hexane + 1-hexanol > hexane + 2-methyl-2-propanol > hexane + 1-propanol. In case of fig. 1(a) of hexane + 1-propanol mixtures, the negative V^E values show minimum around 0.3 mole fraction. This trend of V^E values of the three systems might be an indication of the three different types of alkanes. The negative V^E values in the mixtures of the system hexane + 1-propanol, but the positive V^E values shows in the other two binary systems. In our recent studies a similar trend in V^E values of higher alcohols + alkanes was observed by a number of workers. The alcohols are highly structured polar liquids and addition of non-polar alkanes results in the breaking of hydrogen bonds, contributing a positive effect to V^E . This has been found so with other systems but a contrasting was noticed where hexane was added to 1-propanol. In case of the hexane molecules, it was partly or fully interstices of polynuclear ring when mix with the alcohols of higher alkanol molecules formed by H-bonding. Thereby the negative contribution of which were dominating over the positive contributions. In case of other systems positive contribution dominate over the negative contribution as reflected in the V^E values.

The observed V^E values of the mixtures under investigation can be explained in terms of the following contributions:

- (1) Effect due to differences in the chain length of the alkanols,
- (2) Dipole-induced dipole interaction between the unlike polar and non-polar molecules,
- (3) Geometric effect due to differences in molar volumes of the component molecules,
- (4) Electronic factors that cause repulsion between the component molecules,
- (5) Tendency of self-coiling of the linear hydrocarbon molecules,

The excess molar volumes of the binary mixtures under investigations may be considered to be the resultant of the above-mentioned competing interactions of the component molecules. Except hexane, all the components are polar compounds; the value of dipole moment (μ) being 1.68, 1.68, 1.21 D for 1-propanol, 2-methyl-2-propanol, and 1-hexanol, respectively. Addition of hexane molecules causes dissociation of the associated alcohol molecules resulting in expansion in volume. Further, both the alcohol and the alkanes being bulky and electron releasing molecules, there would have unfavourable interactions between them and positive V^E is expected. There may, however, be dispersive force of attraction due to the permanent dipole of the alcohol and induced dipoles of the alkane molecules oscillating in phase. This would have very weak effect in volume contraction. All the mixtures

have, therefore, positive values of V^E . The value of dielectric constants (ϵ) being 1.9, 18.3, 10.9, 13.3 for hexane, 1-propanol, 2-methyl-2-propanol, and 1-hexanol, respectively. The values of the index of refraction (ND) at room temperature were 1.372, 1.375, 1.383, and 1.416 for hexane, 1-propanol, 2-methyl-2-propanol, and 1-hexanol respectively. The values of molecular magnetic rotation power in the same magnetic field (Q_m) being 5.66, 3.372, 4.91, and 6.89 for hexane, 1-propanol, 2-methyl-2-propanol, and 1-hexanol respectively when the value of wave length (λ) is 589μ .

As far the magnitude of V^E , it has been observed that V^E increases with increasing chain lengths [28] and increasing alkane size [29]. The magnitudes of the V^E values of the mixtures were in the order hexane + 1-hexanol > hexane + 2-methyl-2-propanol > hexane + 1-propanol. The observed low V^E values of hexane + 1-propanol may be explained in terms of differences in molar volumes of the components and tendency of self-coiling of hydrocarbon molecules. The molar volumes of hexane, 1-propanol, 2-methyl-2-propanol, and 1-hexanol at 298.15K are, respectively, 131.5324, 75.1156, 94.0490, 124.9144 $\text{cm}^3 \text{mole}^{-1}$.

3.3 Discussion on viscometric behavior of the mixtures

The viscosity coefficient of the binary mixtures of hexane + 1-propanol, 2-methyl-2-propanol and + 1-hexanol at 298.15, 303.15, 308.15, 313.15 and 318.15K have been calculated.

Discussion of the viscosity coefficient of binary liquid mixtures starts from the concept of 'ideal' solution with a view to considering a particular system departing from ideal behaviour. The viscosity coefficient of the ideal mixture is represented by the equation,

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 \quad (2)$$

and deviation from the ideal value is expressed in terms of excess viscosity, η^E as

$$\eta^E = \eta_{\text{mix}} - \exp(\sum x_i \ln \eta_i) \quad (3)$$

The excess viscosities of the mixtures at different compositions have been presented in Fig. 3. Similar type of variation of η values of alkane + alcohol mixture was interpreted [30] as due to the dissociation of cyclic association present in pure alcohols to give linear monomers. Our views were also in general agreement with their conclusion.

Grunberg and Nissan [31] suggested an expression (4) for the estimation of viscosity coefficient and strength of interaction between the components of a binary mixture expressed as,

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d \quad (4)$$

Where, the d was proportional to w/RT (w is the interchange energy) and may be regarded as an approximate measure of the strength of interaction between the components. The values of d were generally calculated at $x_1=0.5$ and used to calculate the viscosity coefficient of the mixture at all compositions.

The excess viscosities η^E and interaction parameter d , were majority negative for all the mixtures of hexane + 1-propanol, +2-methyl-2-propanol, and + 1-hexanol at all the temperatures. Nigam and Mahl [32] observed that (i) if $\eta^E > 0$ and the strength of interaction $d > 0$ and the magnitude of both is large, than strong specific interaction would be present, (ii) if $\eta^E < 0$ but $d > 0$ then a weak specific interaction would be present, and (iii) if $\eta^E < 0$ and $d < 0$ and the magnitude of both are large, then specific interaction would be absent. In the present investigations, both the η^E and d values were moderately negative for all the mixtures at all the temperatures. This should indicate the absence of specific interaction between the components resulting in positive V^E for all the systems. Our V^E results were, however, positive for hexane + 2-methyl-2-propanol, + 1-hexanol, and sigmoid for hexane + 1-propanol mixtures. The geometric effect due to differences in molar volume of the component molecules, perhaps, predominates for hexane + 1-propanol mixtures resulting in negative V^E . The V^E values, thus, gradually increases with the chain length [5] of alkanols and becomes positive for mixtures.

3.4 Discussion on the free energy of viscous flow

The free energy of activation ΔG^\ddagger for the flow process calculated by equation (5) of Eyring [33,34],

$$\eta = \frac{hN}{V} \exp \left[\frac{\Delta G^\#}{RT} \right] \quad (5)$$

The values of $\Delta G^\#$ were positive throughout the composition range for all the mixtures at all the experimental temperatures. The x_1 vs. $\Delta G^\#$ curves for the hexane + 1-propanol, + 2-methyl-2-propanol + and 1-hexanol mixtures were slightly concave in nature. In the present investigation, at 298.15K the minimum values of η^E have been found to be -0.1664 (at $x_1=0.40$), -1.2131 (at $x_1=0.20$), and -0.5437 (at $x_1=0.10$), for the hexane + 1-propanol, 2-methyl-2-propanol and + 1-hexanol mixtures respectively. Thus the values of $\Delta G^\#$ were in the same order and consistent with the η^E values.

The values of $\Delta G^{\#E}$ have been calculated from equation

$$\Delta G^{\#E} = \Delta G^\# - (x_1 \Delta G_1^\# + x_2 \Delta G_2^\#) \quad (6)$$

Where, $\Delta G^\#$ is the free energy of the mixtures and $\Delta G_1^\#$ and $\Delta G_2^\#$ are the free energies of the pure components 1 and 2 respectively. The values of $\Delta G^{\#E}$ have been shown in the figures 6. It is further observed that the $\Delta G^\#$ increases with the increase of temperature for all the systems at all the compositions. Our observations indicate that the flow process was facilitated by the mixing process. This view was also evident from the values of η^E and d , which were also maximum negative for the mixtures.

Table 1. Calibration constants (A and B) of the viscometer-1 and viscometer-2

	Temperature (K)	A $\times 10^{-3}$	B
	Viscometer- 1	298.15	3.51
303.15		3.51	-2.2841
308.15		3.51	-2.3527
313.15		3.46	-3.5941
318.15		3.41	-3.7967
Viscometer- 2	Temperature (K)	A $\times 10^{-3}$	B
	298.15	3.5	-1.1803
	303.15	3.49	-2.1011
	308.15	3.47	-2.2659
	313.15	3.43	-3.1758
318.15	3.36	-4.5070	

Table 2. Coefficients A_j of Redlich–Kister Eq. (1) and the corresponding standard deviations (s) of all the binary systems

Temperature/K		A_0	A_1	A_2	A_3	A_4	S
Hexane+1-propanol	298.15	-3.4091	-5.4091	1.6123	-0.4685	-1.6636	0.00356
	303.15	-3.2885	5.3271	1.3730	-0.2307	-1.0768	0.00446
	308.15	-3.2460	5.1983	1.6107	0.1398	-1.2950	0.00633
	313.15	-3.1221	5.1042	1.3861	0.1006	-0.8359	0.00583
	318.15	-3.0668	5.0131	1.5800	0.4603	-0.8787	0.00538
Hexane+2-methyl-2-propanol	298.15	8.3186	-5.1404	-0.9851	-0.1399	2.1457	0.00577
	303.15	8.4549	-5.1099	-0.6120	-0.2439	1.7254	0.00267
	308.15	8.7932	-5.2049	-0.6834	-0.2935	1.8407	0.00732
	313.15	9.1427	-5.3336	-0.5327	-0.4177	1.8537	0.00705
	318.15	9.6486	-5.5473	-0.8626	-0.5767	2.3843	0.00238
Hexane+1-hexanol	298.15	10.5480	-0.2116	1.1209	-0.2061	-0.5516	0.00563
	303.15	10.7768	-0.0503	1.6383	-2.0949	-1.8887	0.00676
	308.15	10.9337	0.0034	1.4492	-2.6179	-1.2752	0.00470
	313.15	11.2459	-0.6529	1.0422	-1.0812	0.5511	0.00380
	318.15	11.5909	-0.9632	1.1101	-1.3088	1.2793	0.00602

The applicability of two molecular theories in predicting thermodynamic properties was tested. In particular the experimentally determined dependence of the excess enthalpy on pressure of some binary alkane + alkane and alcohol + alkane mixtures was used in this investigation. A consistent description of the experimental results of the alkane + alkane mixtures was possible using a modified Prigogine-Flory-Patterson free volume theory, which accounts for the short range order observed for alkanes. To the alcohol + alkane mixtures the real associated solution model has been applied in order to take into account the volume change upon mixing due to hydrogen bonding of

the alcohol. This model, however, was found to be insufficient for describing quantitatively the pressure dependence of the excess enthalpy.

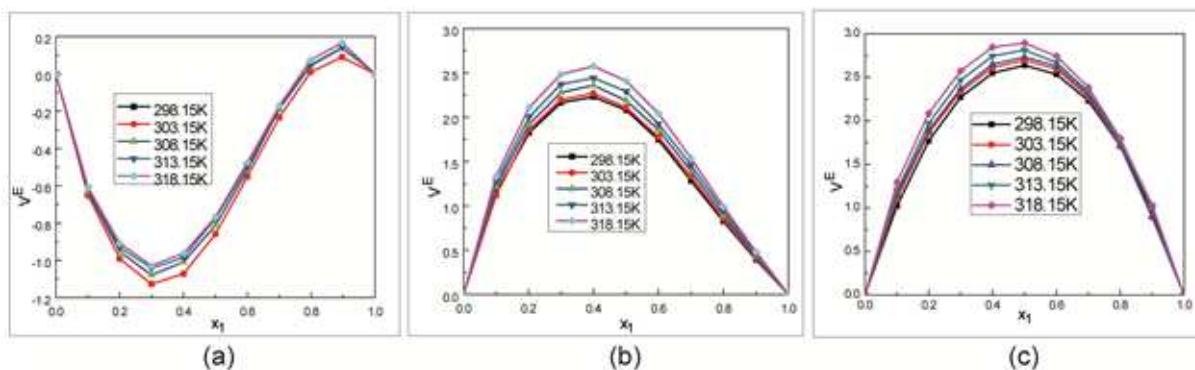


Figure 1. Excess molar volume, V^E of (a) hexane + 1-propanol, (b) hexane + 2-methyl-2-propanol, and (c) hexane + 1-hexanol, at different temperatures and compositions

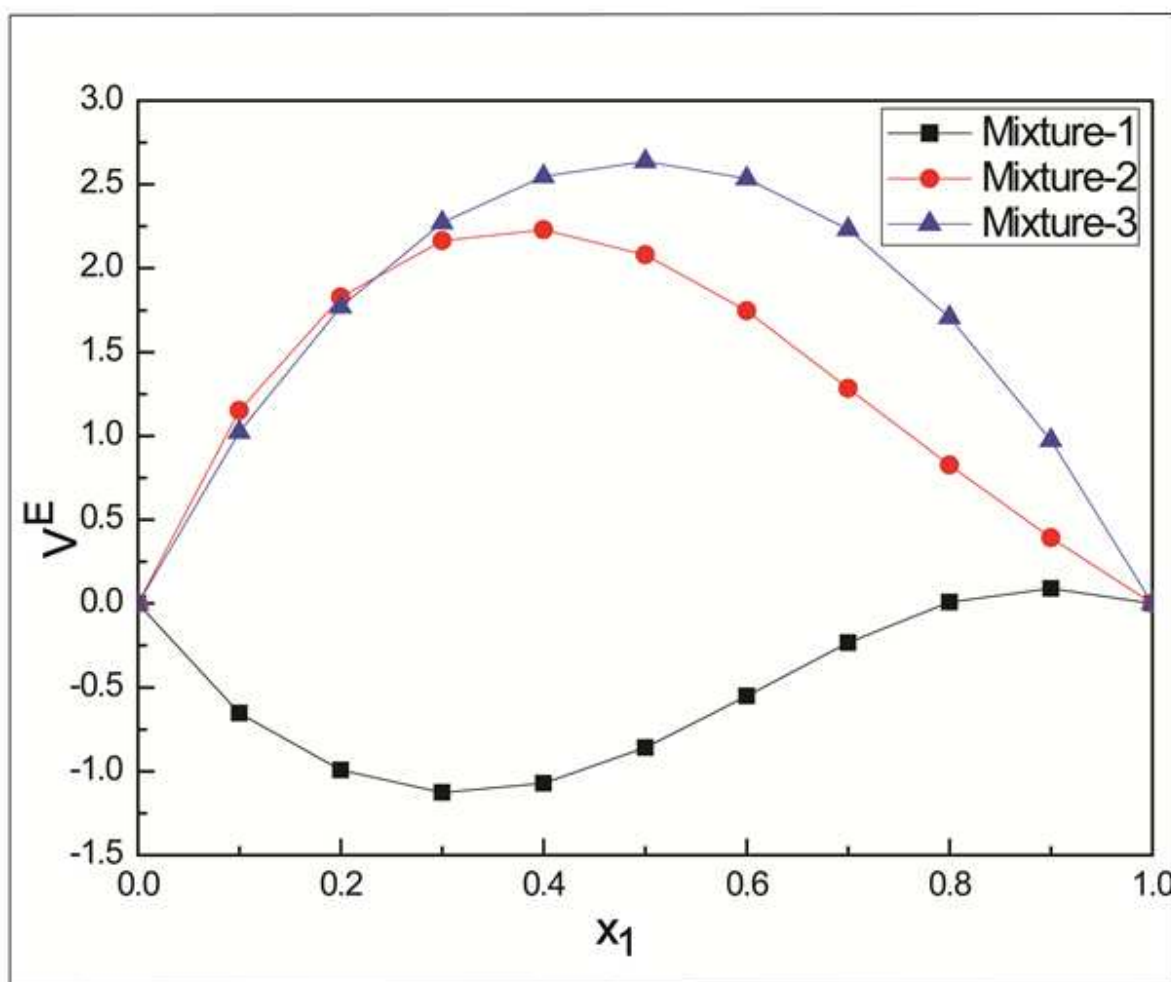


Figure 2. Excess molar volume, V^E of our three different systems at 298.15K temperatures and different compositions

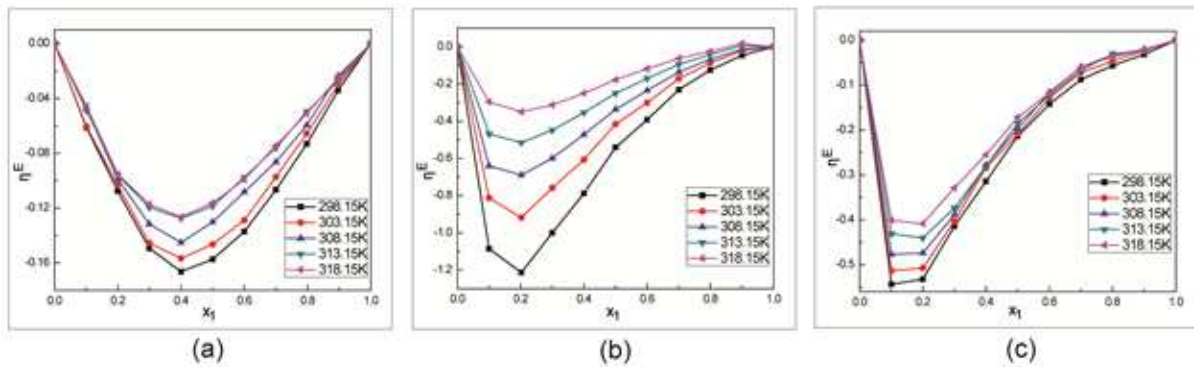


Figure 3. Excess viscosity coefficient, η^E of (a) hexane + 1-propanol, (b) hexane + 2-methyl-2—propanol, and (c) hexane + 1-hexanol, mixtures at different temperatures and compositions

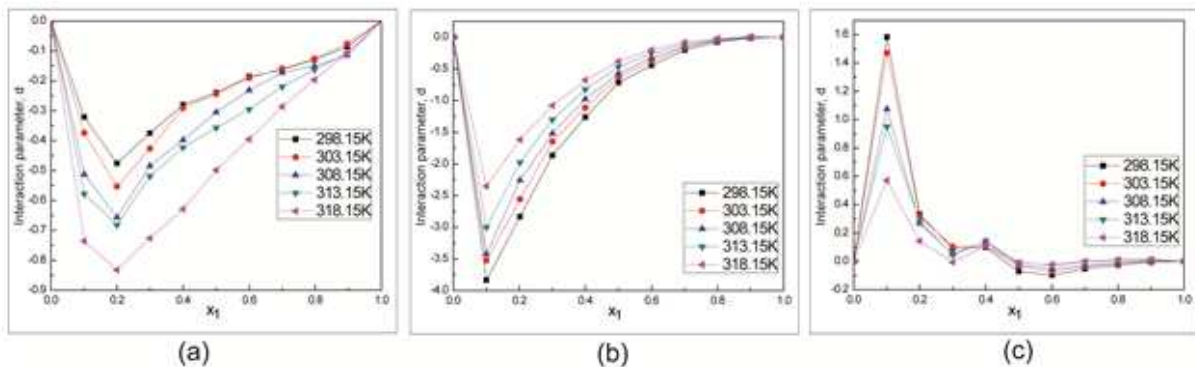


Figure 4. The interaction parameter, d of (a) hexane + 1-propanol, (b) hexane + 2-methyl-2-propanol, and (c) hexane + 1-hexanol mixtures at different temperatures and compositions

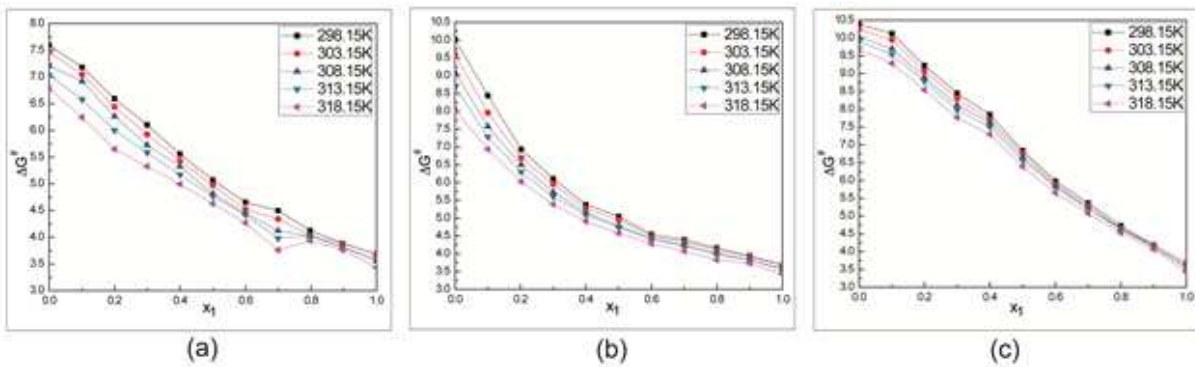


Figure 5. Free energy of activation, $\Delta G^\#$ of viscous flow of (a) hexane + 1-propanol, (b) hexane + 2-methyl-2-propanol, and (c) hexane + 1-hexanol mixtures at different temperatures and compositions

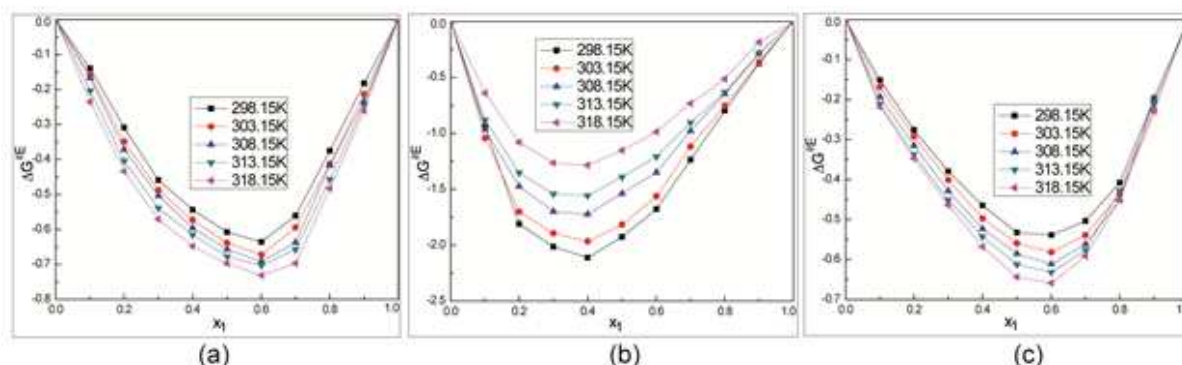


Figure 6. Excess free energy of activation, $\Delta G^{\#E}$ (kJ mol^{-1}) of viscous flow of (a) hexane + 1-propanol, (b) hexane + 2-methyl-2-propanol, and (c) hexane + 1-hexanol mixtures at different temperatures and compositions

CONCLUSION

The excess molar volumes V^E and the excess viscosity coefficient η^E of the binary mixtures of hexane + 1-propanol, + 2-methyl-2-propanol, and + 1-hexanol have been determined at five different temperatures, viz., 298.15, 303.15, 308.15, 313.15 and 318.15K over the entire range of compositions. The values of V^E of the hexane + 2-methyl-2-propanol, and hexane + 1-hexanol mixtures were positive over the entire range of composition. The V^E values for the hexane + 1-propanol mixtures were sigmoid, being positive at higher mole fractions (x_1) and negative at lower mole fractions x_1 of hexane. The magnitudes of the V^E values of the mixtures were in the order hexane + 1-hexanol > hexane + 2-methyl-2-propanol > hexane + 1-propanol. The observed values of the V^E for the mixtures can be explained in terms of the (i) dissociation of the associated polar molecules, (ii) dipole-induced dipole interaction between the polar and non-polar molecules, (iii) repulsive electronic force between the components and (iv) geometric effect due to differences in molar volumes. The viscosity coefficients η of all the above mixtures at all the five different temperatures have also been determined. The viscosity coefficients of the polar-non-polar mixtures, quite expectedly, show considerable deviation from ideal behaviour. The excess viscosities η^E are maximum negative and some are positive for all the mixtures at all the temperatures. The interaction parameter d was calculated from the equation of Grunberg and Nissan and was found to be maximum negative and some are positive for all the mixtures at all the temperatures. Negative values of both η^E and d have been explained in the light of the observation of Nigam and Mahl. Free energy for viscous flow $\Delta G^\#$ and excess free energy for viscous flow $\Delta G^{\#E}$ were calculated. The viscosity coefficients have also been computed from the equation of Bloomfield and Dewan. The results show that while the theoretical values of V^E do not agree with the experimental results, there are agreements between the calculated and experimental values of the viscosity coefficient.

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