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Viscometric Investigations on Molecular Interactions of some Selected Hydroxy Substrates in Water

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Abstract : The density and viscosity of solutions of methanol, ethanol, glucose and sucrose in distilled water at various temperatures were reported and compared with the available literature data. Data obtained was used to understand the interactions of substrates in solution. Influence of concentration of substrates and salts on strengthening or weakening of these interactions was evaluated. Apparent molar volumes were estimated from density data of different systems. The presence of various polar groups in the molecules showed varying interactions and there by the viscosity also varies. The results reveal that the molecular interactions strongly depend on the polarity and the substituents attached to the hydroxyl groups. Influence of nature of substrates and the other ions commonly present in water is discussed. Also, we have analyzed the relations between alcohols and their properties using a data analysis technique, Formal Concept Analysis (FCA).
Keywords: Viscosities, Apparent molar volumes, Ethanol-water mixture, Methanol-water mixture, Formal concept analysis, concept lattice.

Introduction

Density, viscosity, and surface tension of liquids are known as significant physicochemical properties in both natural and industrial processes. In view of the significance of water as a reference substance in viscometric studies, the establishment of standard values and investigations on the influence of various substrates dissolved in water is one of the important topics of research for a long time. Studies on densities, viscosities and molar volumes along with their respective excess properties in liquids and liquid mixtures is essential to understand the molecular interactions between unlike molecules, to develop new theoretical models as well as engineering applications in the process industries. The viscosity depends on temperature, pressure and the type and composition of the material. The measurement of viscosity is significant importance in both industry, which allows distinguish directly the quality of the final product such as lubricating oils, adhesives, fuels, paints**,** and so on[1.]

Studies involving density and viscosity measurements are important for elucidation of molecule-solvent and solvent-solvent interaction in mixed solvent systems[2-4]. These interactions can be fully understood from experimental studies like density, viscosity, refractive index, sound velocity *etc*. When electrolytes are added in solvent mixtures, the existing structure of solvent mixtures affects and it changes to another structure.

Molecular interactions in solution have been studied by many workers[5-10]. Volumetric behaviors of electrolyte solutions provide information about various molecular interactions[11-14]. Recently various binary mixtures in the presence of nitrobenzene have been studied [15].

Experimental

All the glassware used were of Borosil make and precalibrated. Densities of different solutions were measured using density bottles (10 mL; Riviera make). Weighing was done on electronic balance (Schimadzu). Solvent mixtures of ethanol-water (v/v) and methanol-water (v/v) were prepared by mixing 10, 20, 40 and 60 mL ethanol in water to make total 100 mL solution in standard volumetric flasks. Solutions of potassium salt were prepared in ethanol-water solvent mixture by dissolving accurately weighed salt in it. Viscosities of solutions were measured by using Ostwald's viscometer (Borosilicate Glass make) at constant temperature (303.15 K) by measuring flow times for ternary solutions and solvent mixtures.

Results and Discussion

According to Fort and Moore[16], An increase in viscosity leads to stronger solutes interactions. The variation in excess viscosity gives a quantitative estimation of the strength of intermolecular interactions; and these values can be explained by considering two factors. One is the difference in size, and shape of the component molecules and the loss of dipolar association in pure compound that may lead to a decrease in viscosity. The other factor is the specific interactions between unlike components such as hydrogen bond formation and charge transfer complexes which may cause increase in viscosity in mixtures over that found in pure components. The former effect produces negative deviation in excess viscosity whereas the latter effect produces positive deviation in excess viscosity. Similarly, Petek et al[17] explained the predominance of expansion in volume, caused by the loss of dipolar association and difference in size and shape of component molecules, over contraction in volumes, due to the dipole-dipole and dipole-induced dipole interactions.

A mixture of methanol or ethanol and water by volume has a higher viscosity. Since the viscosity of alcohol-water mixtures passes through a maximum at this concentration, the viscosity does change significantly with the concentration and strongly depends on molecular weight of the solute, the presence of electrolytes and the nature of substituents in solutes' structures.

The results clearly indicated that the viscosity of ethanol is superior to methanol at equal molar volume due to the larger molecular weight. Fig.5 also indicates the degree of interaction between alcohol and water. When the percentage of alcohol is less the hydrogen bonding is predominant between the oxygen atom of water and hydrogen atom of alcohol. At low concentrations of alcohol (*i.e.* more dilution), the viscosity is less and there by the flow rate increases rapidly when the solution contains 3:2 ratio of water to alcohol. But interestingly the hydrogen bonding is less with an increase in percentage of alcohol as more amount of alcohol surrounds to water molecule. At the higher concentrations of alcohol, it is clear that there won't be any hydrogen bonding further and this leads to faster flow rate.

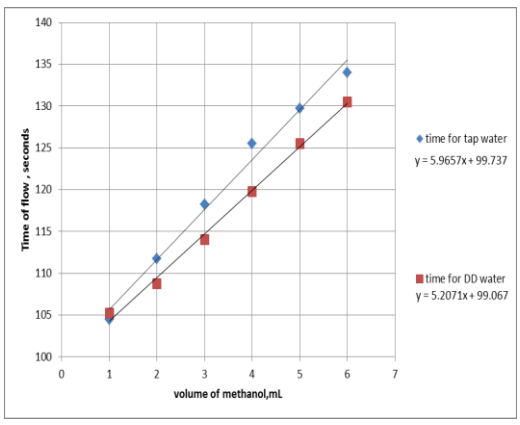

Fig.1 Comparison of flow rates of methanol

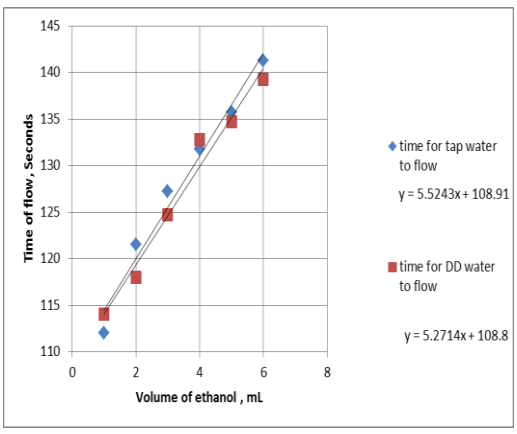

Fig.2 Comparison of flow rates of ethanol

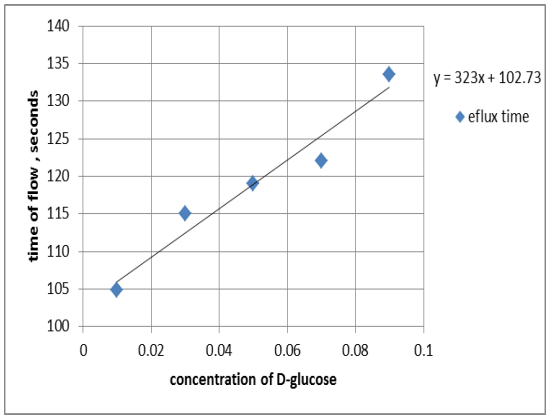

Fig.3 flow rate of D-glucose in distilled water

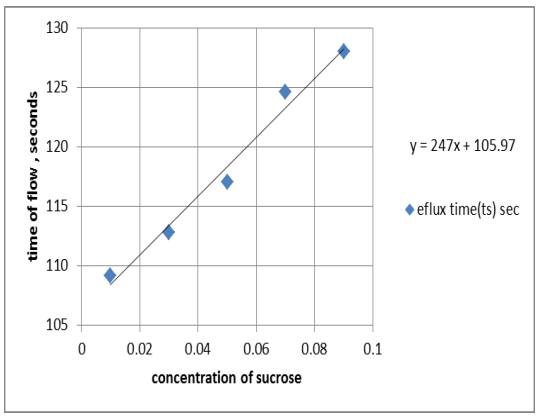

Fig.4 flow rate of Sucrose in distilled water

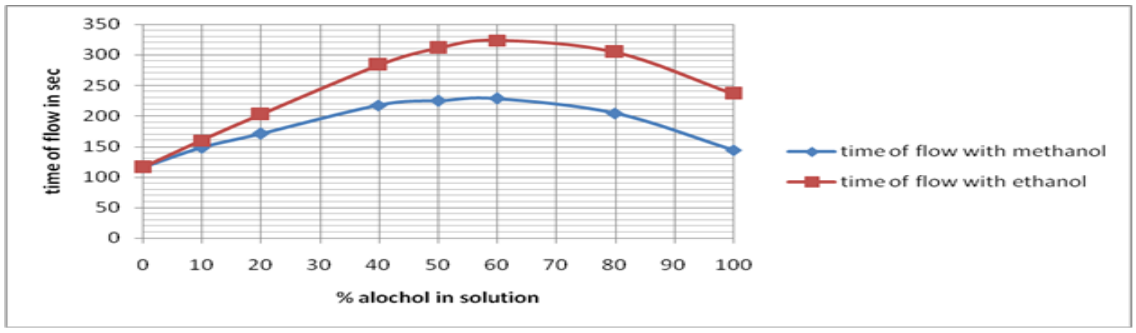

Fig. 5 Change in time of flow of alcohol with an increasing percentage of alcohol

Formal Concept Analysis (FCA): This is a mathematical framework introduced by Wille in early 1980's for the task of data representation and exploring the relations among the data items[18]. FCA receives the input data in the form of matrix representing the elements (objects) of the domain in rows and properties (attributes) of the objects as columns. Each cell of the matrix represents the relation between the elements and their properties. In the classical setting, this relation is binary and hence the matrix contains Boolean values. A cell value 1 indicates that the element has the corresponding property. A null value indicates the absence of the property. This matrix is known as formal context. From this formal context, FCA identifies: a set of object and attribute pairs known as concepts, a complete lattice structure known as concept lattice that represents the hierarchical ordering relation among the concepts and dependencies among the attributes represented in the form of attribute implications. For a detailed discussion on the fundamentals, mathematical notations and applications of FCA, readers are referred to[19-23].

We have used FCA for analyzing the 5 different alcohols of this study and their properties i.e. molecular weight, vapor pressure, and viscosity. For this purpose, first we have performed the conceptual scaling on the values of these three properties as given in the following Table-1. Considering these scales, we have represented the binary relation between the alcohols and each of these three properties scales as a formal context shown in the following Table 2.

Table 1: Scaling on the alcohol properties

Property	Scale	Units
Molecular weight	M1	31-45
	M2	46-60
	M3	61-75
	M4	76-90
Vapor Pressure	VP1	0-3.0
	VP2	3.1-6.0
	VP3	Above 6.0
Viscosity	V1	0-1.9
	V2	2.0-3.9

Table 2: Formal context of alcohols and their scaled properties

	M1	M2	M3	M4	VP1	VP2	VP3	Miscibility	V1	V2
Methanol	1						1	1	1	
Ethanol		1				1		1	1	
n-Propanol			1		1			1	1	
n-Butanol			1		1					1
n-Pentanol				1	1					1

FCA on the context shown in Table 2 has produced 11 formal concepts. Fig. 6 shows the concept lattice obtained from this context. Each node of the structure represents a concept. However we have followed reduced labeling for better visualization[21]. When a node is shown with an attribute, then that attribute is also attached to the nodes in its descending path. Similarly when a node is shown with an object, then the nodes in its ascending path also contains this object. From Figure 1, we can observe that Ethanol has the properties: VP2 (Vapor pressure in the scale 3.1 to 6.0), M2 (Molecular weight 46-60) from node 6 and from node 3 the properties Miscibility and V1 (Viscosity in the range 0 to 1.9). We can understand the relations between the other nodes similarly. Blue color to the upper semi-circle indicates the presence of attribute and the black color in the lower semi-circle indicates the presence of object in the concept represented by the corresponding node. The top and bottom nodes (node 1 and node 11) are called as unit and zero concepts. Unit concept represents all the objects in its objects set and null in its attributes set. The zero concepts represent all the attributes in its attributes set and null in its objects set.

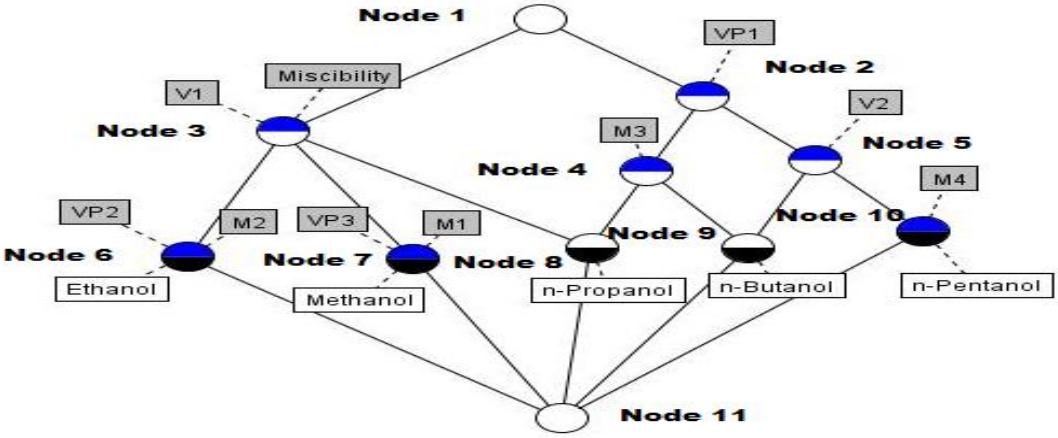

Fig.6: **Concept lattice of alcohols and their scaled properties**

Along with the concept lattice, FCA on the formal context also produces a set of attribute implications, narrating the dependencies between the attributes[20,22]. Among these implications, we have considered the implications with 100 % confidence and non - zero support count. Table 3 lists all these implications.

Table 3: Attribute implications with 100% confidence and non-zero support

S.No	Implication rule	Support
1	V1 ==> Miscibility	3
2	Miscibility ==> V1;	3
3	V2 ==> VP1	2
4	M3 ==> VP1	2
5	M1 ==> VP3 Miscibility V1	1
6	M2 ==> VP2 Miscibility V1	1
7	VP2 ==> M2 Miscibility V1	1
8	VP3 ==> M1 Miscibility V1	1
9	VP1 Miscibility V1 ==> M3	1
10	M4 ==> VP1 V2	1

From these association rules, we can understand that the alcohols (methanol, ethanol, *n*-propanol) that have miscibility also have viscosity in the range (0-1.9) and vice versa. We can observe that the alcohols with viscosity values 2.0 to 3.9 have the vapor pressure in the range 0 to 3.0. This observation is supported by two alcohols, *n*-butanol and *n*-pentanol. From the third implication, we can understand that the alcohols with molecular weight 61-75, have the vapor pressure in the range 0 to 3.0. This observation is supported by *n*-propanal and *n*-butanol. In the same manner, remaining implications can be interpreted and understood.

Conclusions

The nature and degree of molecular interactions in different solutions depend upon the nature of the medium, the structure of the solute molecule and also the extent of solvation taking place in solution.

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