Association Behavior of Mono, Di and Tri-hydric Alcohols with Three Carbon Skeleton in a Straight Chain

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Received June 21, 2014; Revised July 26, 2014; Accepted July 31, 2014

Abstract Association behavior of mono, di and tri-hydric alcohols having three carbon skeleton in a straight chain was studied based on surface tension (γ) data, EÖTVÖS constants (k), order of association (x), hydrogen bond acceptor (H_a)-donor (H_d) counts and Trouton's rule. It is to be understood from the title that alcohols used were 1-propanol, 2-propanol, 1,2-propanediol, 1,3-propanediol and glycerol.

Keywords: surface tension, associative behavior, EÖTVÖS constants, 1-propanol, 2-propanol, 1,2-propanediol, 1,3-propanediol and glycerol

Cite This Article: R. Sanjeev, V. Jagannadham, Adam A. Skelton, and Arijit Das, "Association Behavior of Mono, Di and Tri-hydric Alcohols with Three Carbon Skeleton in a Straight Chain." *World Journal of Chemical Education*, vol. 2, no. 3 (2014): 39-41. doi: 10.12691/wjce-2-3-2.

1. Introduction

The putative study on molecular association or dimerization of benzoic acid was reported more than a century ago [1] and later in 1966 [2]. The study of molecular association or dimerization of organic molecules by titration method is a generally accepted practice in graduate and undergraduate physical chemistry laboratory especially in the case of carboxylic acids. Much laboratory work had been performed by Moelwyn-Hughes and his associates [3,4] on acetic acid and propionic acids distributed between water and several organic solvents in which these acids dimerize. The same study may not be practicable for molecules other than carboxylic acids by simple titration method. The method of Ramsey-Shields-Eötvös equation [5,6] was a successful practice to study the molecular associations based on dependence of surface tension on temperature. The present article is based on surface tension data, EÖTVÖS constants (k), order of association (x), hydrogen bond acceptor (H_a)-donor (H_d) counts and Trouton's rule is a major breakthrough from our laboratory hither to were not reported earlier in literature.

2. Experimental Data Source

The surface tension data of the alcohols used in the present work is from references [7] and [8]. Thermo chemical data is from reference [9]. Other physical

constants like density, molecular weight and boiling points are from standard sources.

3. Discussion

A molecule in the bulk of a liquid is completely surrounded by other molecules; therefore it is attracted equally in all directions. While a molecule on the surface has an attraction inward because the number of molecules per unit volume is greater in liquid than in vapor. Due to this inward pull, the surface of the liquid always tends to contract to have minimum possible area. As a result of this tendency to contract, a surface behaves as if it was in a state of tension and is called surface tension (γ).

Eötvös [6] had suggested the following equation that explains the effect of temperature on surface tension (γ):

$$\gamma \left(\frac{M}{\rho}\right)^{2/3} = k(t_c - t) \tag{1}$$

Where 'M' is the molecular weight of the liquid, 'p' is the density, 't_c' is the critical temperature, 't' is temperature and 'k' is the Eötvös constant. For most liquids 'k' works out to be about 2.12 in the *cgs* system. Such liquids are considered to be ideal liquids and they have identical molecules in the vapor and liquid states. Further the study on Eötvös equation was made by Ramsay and Shields [5,6], who found that the experimental results for a number of liquids could be better explained by the relation:

$$\gamma \left(\frac{M}{\rho}\right)^{2/3} = k(t_c - 6 - t) \tag{2}$$

This equation indicates that the surface tension becomes zero at a temperature 6°C below the critical point. Ramsay and Shields had also found that the value of 'k' works out to be 2.12 for most of the liquids which are normal and non-associative. For certain liquids like water, alcohols and carboxylic acids which contain OH group the 'k' values are not only less than 2.12 but vary with temperature. The deviation was attributed to the association of these liquids. However some substances though they do not contain OH or carboxylic groups like succinic nitrile gave a very low value of 0.56 [10] and substances like glyceryl tristearate had a very high value of 6.0 [11]. This may be due to the fact that in addition to association, the 'k' value may be affected by the shape and orientation of the molecules in the surface of the liquid. Though the less than 2.12 value of Eötvös constant (k) may be an indication of the liquid to be associated preferably through hydrogen bonding, but the change in 'k' with temperature certainly has no simple quantitative meaning [12].

Calculation of Eötvös constant (*k*): Rewriting equation 2, we get

$$\gamma \left(\frac{M}{\rho}\right)^{2/3} = (kt_c - k6) - kt$$
 (3)

$$\gamma = C - \frac{k}{\left(\frac{M}{\rho}\right)^{\frac{2}{3}}}$$
 (4)

Where C =
$$(kt_c - k6) / \left(\frac{M}{\rho}\right)^{2/3}$$

' γ ' versus 't' yields a straight line with a negative slope =

$$\frac{\kappa}{\left(\frac{M}{\rho}\right)^{\frac{2}{3}}}$$

Thus
$$k = \text{slope} \cdot \left(\frac{M}{\rho}\right)^{\frac{2}{3}}$$
.

The slope values are from references [7] and [8]. Hence, the Eötvös constant (k) values are obtained.

Based on the explanation given by Glasstone [12], the order of association of associative liquids could be calculated as follows:

Let 'x' be the order of association of associative liquid Therefore 'x' of its molecules have formed one associated molecule, the molecular weight of the substance in the liquid state will be 'xM'.

Taking the equation (2)

$$\gamma \left(\frac{M}{\rho}\right)^{2/3} = k(t_c - 6 - t)$$

This gives an observed value of k. And for associated molecules, to get order of association, forcing the value of k to be equal to 2.12, the equation would be:

$$\gamma \left(\frac{xM}{\rho}\right)^{2/3} = 2.12(t_c - 6 - t)$$
 (5)

Dividing equation 5 by the equation 2

$$(x)^{2/3} = \frac{2.12}{k} \tag{6}$$

Or

$$x = \left(\frac{2.12}{k}\right)^{\frac{3}{2}} \tag{7}$$

Thus knowing the value of k from the temperature dependence of surface tension as explained above the order of association could be obtained.

The values of Eötvös constants (k) and order of association (x) are presented in Table 1. In all the cases the value of k less than 2.12 (Table 1) is a strong indication of association of these molecules preferably through hydrogen bonding as shown in the scheme 1

$$\begin{array}{c} H \\ CH_2 \\ CH_2O-H & OCH_2 \\ \hline \\ 1\text{-propanol} \\ \end{array} \begin{array}{c} CH_2 \\ CH_3 \\ \hline \\ 1\text{-propanol} \\ \end{array} \begin{array}{c} CH_3 \\ CH_3 \\ \hline \\ CH_3 \\ \hline \\ 1\text{-propanol} \\ \end{array} \begin{array}{c} H \\ CH_2 \\ \hline \\ CH_3 \\ \hline \\ CH_4 \\ \hline \\ CH_5 \\ CH_5 \\ \hline \\ CH_5 \\ CH_5 \\ \hline CH_5 \\ \hline \\ CH_5 \\ CH_5 \\ \hline \\ CH_5 \\ \hline \\ CH_5 \\ CH_5 \\ \hline \\ CH_5 \\ C$$

Taking two molecules is justified because their order of association (x) is close to 2 for all the molecules (Table 1, scheme 1). This is again reflected on their hydrogen acceptor/donor sites (H_{ad}) values.

Scheme 1

3.1. Significance of Boiling Points

Here it is worth to discuss about the boiling points of the alcohols. The boiling point of 1-propanol (97°C) is greater than that of propane (-43°C) (Table 1) in spite of the two molecules have the same number of electrons and almost the same shape. The prime reason is that primary alcohols can form hydrogen bonds between two molecules (intermolecular) (scheme 1). In the case of secondary alcohols one would have to compare the boiling point of 2-propanol (83°C) and propane again (-43°C) (Table 1). The boiling point of the secondary alcohol is less than that of the corresponding primary alcohol with the same number of carbon atoms. Though the boiling point of 2propanol is less than that of 1-propanol in spite of their ability to form inter-molecular hydrogen bonding, they have only one hydrogen atom on the oxygen and the oxygen in secondary alcohol is in the middle of the two carbon atoms makes the dipole-dipole interactions less than in 1-propanol in which oxygen is at the end in the

molecule whose dipole-dipole interactions are strong enough. Hence lower boiling points in secondary alcohols compared to the corresponding primary alcohols. The same arguments hold good for 1,2 and 1,3-propanediols where in 1,3-propanediol the two hydroxyl groups are on the terminal carbons makes it high boiling with high degree of dipole-dipole interaction. In the case of glycerol, though it had same number of carbons but the boiling

point is too high 290°C. The reason for this we have attributed that glycerol is a non-ionic kosmotrope (ordermaker) that forms strong hydrogen bonds with neighbouring molecules, resulting in larger molecular aggregates [13]. This is again reflected on the largest hydrogen donor-acceptor ((H_{ad}) value of glycerol (Table 1). This may lead glycerol to have high boiling point.

Table 1. Surface tension (γ) and other data of some mono, di and tri-hydric alcohols Units of ΔH_v in kJ/mol and ΔS_v in J (K.mol)⁻¹

Compound	γ at 25°C (dyn/cm)	mw	ρg/ml	BP (°C)	ΔH_{V}	$\Delta S_{\rm V}$	k	X	H_{a}	H_{d}	$H_{ad} \\$
1-propanol CH ₂ (OH)CH ₂ CH ₃	23.3	60	0.80	97	41	112	1.4	1.9	1	1	2
2-propanol CH ₃ CH(OH)CH ₃	20.9	60	0.79	83	40	112	1.4	1.8	1	1	2
1,2-propandiol CH ₂ (OH)CH(OH)CH ₃	44.8	76	1.04	188	52	114	1.6	1.6	2	2	4
1,3-propandiol CH ₂ (OH)CH ₂ CH ₃ (OH)	45.7	76	1.06	214	58	119	1.6	1.6	2	2	4
glycerol CH ₂ (OH)CH(OH)CH ₂ (OH)	63.4	92	1.26	290	61	108	1.5	1.6	3	3	6
Propane CH ₃ CH ₂ CH ₃				-43.0							

3.2. The Trouton's Rule

 $\Delta S_{\rm v}$ data of the alcohols are from reference [9] and are presented in Table 1. Trouton's rule is of interest in the context of latent heats of vaporization of liquids. It is an empirical rule based on heats of vaporization of a large number of normal liquids at their boiling points. According to this rule the entropy of vaporization is almost the same value, about 85–88 J (K mol)⁻¹, for various kinds of liquids at their boiling points [14]. Abnormal values of Troutons' rule constant suggest abnormal entropy changes during vaporization of concerned liquids. If the Troutons' rule constant for a liquid is more than the limit of 85–88 J (K mol)⁻¹ it suggests association of molecules in the liquid form. In fact the same trend is observed in the case of all the alcohols observed (Table 1).

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