Thermo physical proparties of aqueous solution for water and some alcohols at 298 .15 K

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Received 23 March 2015 ; Accepted 24 May 2015

Abstract

Through Isopiestic method Was discussed in this study solutions for homogenous interactions of water with alcohols (2-Decanol,2-octanol,2-hexanol and cyclohexanol) at 25 c° . Been observed that interactions of water with cyclohexanol more if larger compared with alcohols which have been selected in this study , whereas interactions of water in alcohols increased with increasing the activity of water . The value of Hernys constant for the reaction 2-hexanol with water is much lower so calculated values of molality osmotic coefficients for the reaction of water with alcohol reaction is low and decrease with increasing molality of the mixture . The positive values of excess Gibbs energy of maxing water with alcohols($\Delta_{mix}G^E$) through a strong interference between water molecules and alcohols 2-Decanol,2-octanol,2-hexanol and cyclohexanol .

Keywords: Cyclohexanol : secondary alcohols: Gibbs free energy: physical properties .

الخواص الثرموفيزيائية للمحلول المائي المكون من الماء وبعض الكحولات عند درجة حرارة 298.15 كلفن

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الخلاصة

من خلال طريقة isopiestic ناقشنا في هذه الدراسة المحلول المائي المتجانس لتداخلات الماء والكحلولات (2-هكسانول، 2-ديكانول، 2-اوكتانول، السايكلوهكسانول) عند درجة حرارة 25سيليزي. تم ملاحظة تداخلات الماء مع السايكلو هكسانول اكبر واكثر من تداخلات مع الكحولات التي تم اختيارها في هذه الدراسة حيث ان تداخلات الماء والكحولات تزداد مع زيادة فعالية الماء. ان قيم ثوابت هنري اقل من القيم المولالية المحسوبة لمعامل التناضح للماء والكحولات وتنخفض مع زيادة مولالية المحلول. تم الحصول على القيم الموجبة لفائض طاقة كبس لخليط الماء والكحولات من قوى التداخل. بين جزيئات الماء والكحولات (2-هكسانول ، 2-ديكانول ، 2-اوكتانول ، السايكلوهكسانول).

الكلمات المفتاحية: سايكلوهكسان ، الكحول الثانوي ، طاقة كبس الحرة ، الخواص الفيزيائية.

Introduction

Solubility data of two liquid are needed for many separation applications of aqueous solutions. The solubility of water plays important role in such systems . Previous studies discussed a mixture of water and alcohols. [1, 2], the mixture of water in alcohols not the focus of attention. Accurate melting data represent a big problem in analyzing solutions which contains a few per cent of water molecules . There is a problem about the configuration of homogeneous solution of mixture water with alcohols . [3], by the isopiestic method can be achieved a homogeneous solutions of water in an organic solvent in which water is distributed between vapor and the organic solution. This problem arises because of the contradictions in the water properties in extenuating solutions of previous studies .

The available two liquid mixture data for alcohol with water binary systems,, Where these values are shown in the two studies by [4-5].

In dilute solution the molecular complexity of water with alcohols. Pure water and pure alcohols are linked by hydrogen bonding. There is a difference in the quality of the links, where the aliphatic 2-alcohols with cyclohexanol form linear hydrogen bonds [6-8]. Water in a liquid state make up the bulk three-dimensional network of hydrogen bond [9]. The mixture for water with alcohol ruptures the structure of both results and components in lower complexes of lower dipole those in the pure alcohol and more dynamic in nature and finally you will be less obstruction bonds [6].

The end result will be less hindered in reforming [10]. The average number of molecules of the second article (alcohol) smaller, so it can not be realized for all molecules the first article (water)such as this structure [11].

In this study, the search for water behavior or activity to configure strong bonds through melted in alcohols which can be used as thermodynamic properties . Such research applied in the previous, but in this study we used isopiestic method in a homogeneous mixture of alcohol and water. The addition of such a study to previous studies contribute to the increase of various activities of the water .

Experimental Method

Material 2-Decanol Fluke,(Purity 99.5%), 2-octanol (Purity 99.5%). 2-hexanol (Purity 99.0%), and cyclohexanol (Purity 99.5%). Was used and dried using anhydrous calcium chloride by placing in desiccator to preserve it from humidity, Where he was studying the density of the mixture at 25c°, Where the results came approach previous studies (Nearly the best by 0. 10 %) [12-15].

The alcohol and water mixture studied by the isopiestic method 298.15 Kelvin [16-18] Water activity know through the use of saturated aqueous solutions at 298.15 K. [19]. Equilibration between of solid phase with saturated salt solution for isopiestic method. The equilibrium for two days immersed in the installed water bath at 298.15 ± 1 ,where the water was determine to alcohol recorded five readings average and accurately 10μg is water per 1 ml .

The activity of the water in alcohol depends on the mixing of water and alcohol, where the solubility ratio 0.1-0.18, the melting of alcohol barely mentioned in saturated salt solutions, because a few water-soluble alcohols , because the salt solution salting occur out [4].

Before using the isopiestic method and before proceeding has been working to make sure the accuracy of the isopiestic method by identifying mixture (water and gasoline), one of the water activities. The water and gasoline mixture value at a temperature of 298 K temperature was 0.0360 ± 0.0009 mol dm^{-3} ; It is close to listed in the source [20] of 0.0349 mol dm $^{-3}$ [21] of 0.0363 mol dm^{-3}. As referred for IUPAC the best value was 0.0350±0.00350moldm^{-3}. [22]

Discussion of Results

Table 1 shows the results of a mixture of water and alcohol with literature values and through the results shown note some of the differences and these differences may date back to the method of preparation of solutions saturated by what has been explained in the introduction Search [3].

Through which the data were obtained from the literature show that the values obtained in this study were higher than the values listed in the [4-5]. The results of the mixture (water and cyclohexanol) of the binary system was higher than the results of the water mixture with other alcohols are described in Table (1) . The melting points of cyclohexanol 298.15 K , where they can expect to cyclohexane and groups consisting addition of water does not cause the formation of hydrogen bonds strong between the mixture molecules (water, alcohols) [23],. The water absorption of alcohol in the process independent of the link to alcohol molecules process, but depends on the extent of mixing alcohol in water. The melting cyclohexanol differs from melting 2-hexanol in the 298.15 K and as the melting 2-hexanol 0.60 and cyclohexanol 3.8 Percent [4] .

Table(1) Solubility of H_2O at unit H_2O in pure alcohol at 298.15K

Alcohol	m/mol kg^{-1}	m/mol kg^{-1}	(lit. values)			
2-hexanol (A)	5.001	4.8^{A}, 4.96^{B}	4.98^{C}, 5.06^{D}	4.99^{E}	4.80^{F}	4.98^{G}
2-octanol (B)	3.833	3.9^{A}, 3.89^{B}	2.00^{C}	2.91^{E}	2.58^{F}	2.80^{G}
2-decanol (C)	3.541	3.2^{A}, 3.61^{B}	3.33^{C}			3.10^{G}
Cyclohexanol (D)	8.890	8.54^{A}	8.73^{C}			

A,B [4]: C,D[5]: G[11] :E,F[14]

Table (2) Mix some alcohols with H_2O as a measure of H_2O activity at 298.15k

	$(m/mol.kg^{-1})$			
A	2-hexanol	2-octanol	2-decanol	Cyclohexanol
0.1559	0.1565	0.0989	0.0765	0.2065
0.2799	0.3859	0.2721	0.1928	0.5751
0.3555	0.6091	0.4362	0.3354	0.8067
0.4799	0.9025	0.6452	0.4415	1.2224
0.5210	0.9633	0.7026	0.5381	1.3528
0.5579	1.1775	0.7765	0.5808	1.5393
0.5901	1.2478	0.8316	0.6138	1.5843
0.6071	1.4186	0.9095	0.713540	1.8889
0.6688	1.6547	1.0988	0.8159	2.0777
0.7983	2.2114	1.3800	1.0700	2.8740
0.8211	2.2611	1.4417	1.2465	3.0328
0.8557	2.3958	1.4932	1.2000	3.1812
0.8971	2.5809	1.5634	1.2980	3.4700
0.9231	2.5994	1.6174	1.3300	3.6559
0.9600	2.8700	1.6994	1.4067	4.1393
0.9901	3.0852	1.7958	1.5046	4.5055
1.0008	3.3515	2.0354	1.69327	5.0066
1.0652	3.1375	2.1968	1.8128	5.6370
1.1002	4.7071	2.6713	2.17883	7.4692

The analysis of practical and the results explained in Table (2) of the mixture of water and alcohol through the equation (1)., [24,25]

$$\ln(a_2/m)= \lambda_0+\lambda_1 m+\lambda_2 m^2 \text{ --------- } (1)$$

Table (3) shows a correlation coefficients mixture of water and alcohol at 298.15 K with relationship of the standard error and relationship of the estimate.

Alcohol	$-\lambda$	$-\lambda 1$	$-\lambda 2$	r	S
2-hexanol (A)	0.594±0.015	0.290±0.010	0.0145±0.0023	0.8990	0.019
2-octanol (B)	0.289±0.012	0.288±0.005	-	0.8995	0.017
2-decanol (C)	0.021±0.015	0.379±0.010	-	0.8831	0.030
Cyclohexanol (D)	0.825±0.015	0.224±0.0090	0.0082±0.0014	0.8848	0.028

Note that (2-hexanol) more interference with water from binary alcohols used in this study, all of which (2-decanol and 2-octanol), where the last show a form of linearly form of Equation . (1) that must be used theory of solution [26], In equation (1) there is a relationship between the coefficients ($G_{22}=\lambda_1$ $RT_{/2}$ and $G_{222} = \lambda_2$ $RT/_3$). They are characterized by excess Gibbs energy contributions and returns to triple because of overlap between alcohol molecules at 298.15 K ,the big or strong interaction between the solute and solvent molecules and clear through negative values (G_{22}), but there is little interaction observed when approaching the solute molecules with each other without the solvent and this shown by positive values(G_{222}) [27] .

Through this mixing note that the values ($g_{22} > g_{222}$) through this behavior there is considerable overlap between the water molecules and the molecules of alcohol At Henry's law [28], Equation (2)

$$\lim_{x\to 0}\left(\frac{a_2}{x_2}\right) = H_{21} \quad \text{---------------} \quad (2)$$

Where :

The Henry's law constants, (H_{21})

The relationship between (H_{21}) with (λ_0) the given equation (3)

$$H_{21} = \frac{\exp(\lambda_0)}{M_1} \quad \text{--------------} \quad (3)$$

Where :

M_{alcohol} = is the molecular weight . In table (4) indicated the Henry's law constant of the literature and a mixture of water and alcohol, as it was noted at interference the water and 2-octanol practically with the Henry's law constant convergent of literature

Table (4) Shows H_{21}(Henry's law constant) in some alcohols in this study at 298.15K

Alcohol	H_{21}	H_{21}(Ref. [14])
2-hexanol	5.95±0.09	6.97
2-octanol	6.03±0.07	6.02
2-decanol	6.45±0.10	
Cyclohexanol	4.78±0.09	

Through the difference between Henry constants note that 2-hexanol with water a few of this is due to the difference in the preparation of saturated solutions and which had previously referred [25] or because of the way isopiestic method as increases Henry the longer the chain of alcohol (increase methylene group) This is shown in Table (4). Through this study, it was observed that the alkyl group has a very important role in the interaction between alcohol and water, (hydrophobic interaction). It was also noted that the (H_{21}) depends on the Gibbs energy ΔG_h^* [29] with an Intersection of (10.0± 0.2) and a slope of (0.24 ± 0.01). Were taken values ΔG_h^* for alcohols of this studied from the source [30].but value of $\Delta G_h^* = -15, 3$ kJ mol$^{-'}$ for 2-decanol from the source [4] and the Gibbs energy into 2-decanol of solution of its vapor condensing from the source [30]. It was also noted that the constant Henry different for the three alcohols and water for water and cyclohexanol because there are a specific reactions. The linear relationship formed as a result of the interaction of water and alcohol depends on the Gibbs energy .

The interpretation of experimental results in Table 2 by the equation. (4),

$$X_2 d\ln a_2 + x_1 \ln a_1 = 0 \text{ ------------- } (4)$$

Where :

x_2 the mole fractions of water, and x_1 the mole fractions of alcohol , (a_2) the activities of water , and (a_1) the activities of alcohol,. The essential form of the Equation (4) is given in Equation (5).

$$1na_1 = -\int_0^{a2} \frac{x_2}{1-x_2} d\ln a_2 \text{ ------------------------------------ } (5)$$

the activity of is given by Equation (6) .

$$\mathrm{Lna}_1, = -M_1 m\left(1+\frac{\lambda_1}{2}m+\frac{2\lambda_2}{3}m^2\right) \text{ -------------------------- } (6)$$

Osmotic coefficient which is defined as in Equation (7)

$$\mathrm{Ina}_1 = M_1 m\varnothing \quad \text{----------------} \quad (7)$$

is given by Equation (8).

$$\phi = \left(1+\frac{\lambda_1}{2}m \mid +\frac{2\lambda_2}{3}m^2\right) \quad \text{-----------------------------} \quad (8)$$

The lim, m→0 $\varnothing$= 1 for a non-electrolyte [31]. Table 5 shows the calculated values practically transactions osmosis of the interaction of water and alcohol. It is accurate up to 6%

Table (5) shows the Osmotic coefficient $\varnothing$, activity coefficient of water in $\gamma 2$,m and excess Gibbs energy of mixing water + alcohol Δ mix. G^E/KJ.mol^{-1}at 298.15K

m/molkg-1	$\varnothing$	in $\gamma 2$,m	$\Delta \mathrm{mix}G^E$/KJ.mol^{-1}
2-hexanol 1	0.965	0.157	0.213
1.5	0.895	0.287	0.391
2	0.823	0.405	0.548
2.5	0.770	0.526	0.677
3	0.715	0.631	0.795
3.5	0.688	0.725	0.898
4.0	0.605	0.911	1.040
2-octanol 1	0.944	0.160	0.278
1.5	0.879	0.289	0.489
2	0.809	0.419	0.683
2.5	0.736	0.576	0.839
3	0.681	0.659	0.973
2-decanol 1	0.911	0.196	0.353
1.5	0.828	0.374	0.597
2	0.739	0.576	0.809

2.5	0.647	0.756	0.977
Cyclohexanol 1	0.967	0.113	0.28
1.5	0.902	0.220	0.44
2	0.863	0.319	0.53
2.5	0.809	0.409	0.69
3	0.772	0.503	0.73
3.5	0.732	0.599	0.82
4.0	0.666	0.766	0.97
4.5	0.592	0.910	1.09
5	0.540	1.052	1.21
5.5	0.498	1.191	1.25
6	0.451	1.299	1.33

The activity coefficient(∅)and activity coefficient of water in γ2,m , was obtained from the osmotic coefficient the relation given by Equation (9) and (10) explained in table (5)..

d[(1 - + md In-γ_2,m --------------------- (9)

In γ_{2},m, = $\lambda_1 m + \lambda_3 m^2$ ---------------------- (10)

$\Delta_{mix}G^E$ of mixing (water and alcohols), on the symmetric scale is given by Equation (11).

$$, \Delta_{mix}G^E = RT\left[x_2 1n\left(\frac{a_2}{x_2}\right) + (1 - x_2)1n\left(\frac{a_1}{1 - x_2}\right)\right] \qquad \text{---------------------} \qquad (11)$$

Through the source[32] was to take advantage of some of the data from water and alcohol overlap table (5) explained the positive values of the surplus energy to squeeze the mixture of water and alcohol.

In Table 5 values can be an explanation for the excess Gibbs energy where the forces of overlap [33]. For mixing process between molecules of materials used in this study . This process is endothermic and interdependence water and alcohol is an exothermic process. The overlap of water molecules the largest overlap water and alcohol molecules or alcohol molecules[34, 2] , These readings show deviations from the Raoult's law [35].

At the end of the work we can say that these systems behave non-ideal behavior, according to the results we reached in this study.

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