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Refractive Properties Of Some Flavored Binary Alcohols At T=298.15-318.15K

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Abstract: Theoretical results of molar refractivity and refractive index for three binary systems, namely 2-propenol + benzyl alcohol, 2-propanol + 2-phenylethenol, and benzyl alcohol + 2-phenyl ethanol, were presented at temperatures of 298.15, 308.15, and 318.15 K and at atmospheric pressure in the concentration range 0.05-0.95, based on the experimental work of Ching-Ta and Chein. The mixing qualities and interactions of these liquids were explored using these data, which were estimated using several models (associated and unassociated). To get the binary coefficients and standard errors, the variances in the refractive index (nD) were analyzed and applied to the Redlich-Kister polynomial equation. A multi-body interaction model developed by McAllister was also used. The molecular interactions of these liquid-state models have been studied and correlated with the behavior of these liquids, which shows that the Lorentz-Lorenz relationship gives good results compared to other models.

***Index Terms*:** RefractiveIndex, MolarRefraction, MacAllister, Flory, Lorenz-Loranz, Interaction, Binary

1. Introduction:

At different temperatures, molar refractivity and index of refraction of liquids are key steps in determining their structure and characterization. Refractive index values, like other thermodynamic data, are useful in engineering calculations for a variety of reasons. The refractive index is used to determine the purity of substances, compute molecular electronic polarizability [1] estimate the boiling point using Meissner's method [2] and calculate other thermodynamic parameters [3,4]. The molar refractivity and index of refraction of flavour alcohols like benzyl alcohol or 2-phenylethanol combined with 2-propanol were investigated in this research. These alcoholic beverages play a significant role in our daily lives. Benzyl alcohol is often used as an embedding medium in fragrance and microscopy [5] as well as a solvent for gelatin [6] 2-Phenylethanol is a basic solvent used in artificial taste and scent. It has protic and self-associated characteristics. Several researchers have recently employed several mixing rules in binary and ternary liquid mixtures to determine the refractive index and test the validity of these mixing rules [7-10]. We present theoretical molar refractivity and index of refraction results for three binary systems, namely 2-Propenol+Benzylalcohol,2-Propanol+2-Phenylethnol, and Benzyl alcohol+2-Phenyl ethanol, at temperatures of 298.15, 308.15, and 318.15 K and atmospheric pressure over the concentration range of 0.05-0.95. The Lorentz-Lorentz(L-L) mixing rule [11] ,1992; Ramaswami and Anbananthan [12] and Glinski [5] models were used to analyse the measured data of Ching-Ta and Chein-Hsiun Tu [13] . The association constant is a changeable parameter in models, [5] whereas the non-associated model [14] is based on liquid additivity. We chose liquids with interacting properties but a high level of technological significance in the chemical industry for this aim. Deviation in index of refraction (nD) has been explored and fitted to a Redlich-Kister type polynomial equation [15] to extract binary coefficients and estimated standard errors using experimental data. The experimental properties were also compared to the McAllister equation [17] which is based on the Eyring theory [17] of absolute reaction rates, and the free energy of activation is additive on a number fraction for liquids.

2. Computational methods:

2.1 Lorentz-Lorentz (L-L) relation:

The Lorentz-Lorentz (L-L) relation can be used to calculate the refractive indices of mixture and density, which are expressed in terms of specific refraction as:

$$\left[\frac{n_m^2-1}{n_m^2+2}\right] = \left[\frac{n_1^2-1}{n_1^2+2}\right]\varphi_1 + \left[\frac{n_2^2-1}{n_2^2+2}\right]\varphi_2 \quad (1)$$

here nm, n1, n2 are the refractive indices of mixture and pure components, 1,2 respectively and $\varphi 1$,$\varphi_2$are the volume fractions of pure components.

2.2 Ramaswami and Anbananthan Model:

The model of Ramswamy and Anbananthan is based on the assumption of refractive index linearity with component mole fraction. When a solute is given to a solvent, the molecules interact in the following manner:

$$A + B \Leftrightarrow AB \quad (2)$$

and the association constant Kas is defined as;

$$K_{as} = \frac{[AB]}{[A][B]} \quad (3)$$

where [A] is the amount of solvent in the liquid mixture and [B] is the amount of solute.

We derive the following results by combining the criterion of linearity in refractive index with composition:

$$n_{obs} = x_A n_A + x_{AB} n_{AB} \quad (4)$$

where xA, xAB, nDA, nDAB, and nD,obs are the mole fraction of A, associate AB's mole fraction, refractive index of A, associate AB's refractive index, and observed refractive index, respectively. The equilibrium reaction in Eq. (4) is incomplete because there are non-related molecules present in the liquid mixture alongside the associated molecules. Eq.(4) takes the form, when the non-associated counterpart is present in the liquid mixture.

$$n_{obs} = [x_A n_A + x_B n_B + x_{AB} n_{AB}] \quad (5)$$

where xB and nD,B are B's mole fraction and refractive index, respectively (non-associated component). However, the equilibrium concentration of pure associate AB may be calculated as follows:

$$K_{as} = \frac{[AB]}{(C_A - [AB])(C_B - [AB])} \quad (6)$$

The starting molar concentrations of the components A and B are CA and CB, respectively. Any value of Kas can be used to compute the equilibrium value of [AB] for any mixture composition, as well as [A] =CA-[AB] and [B] =CB-[AB]. It would now be more practical to substitute molar concentration with activities. As a result, Eq. (6) becomes,

$$K_{as} = \frac{a_{AB}}{(a_A - a_{AB})(a_B - a_{AB})} \quad (7)$$

The activity coefficients of component A, B, and associate AB are represented by aA, aB, and aAB, respectively. Taking equi-molar activities, that is, activities that are equivalent to;

a´A=aA-aAB and a´B= aB-aAB

where a'A and a'B are the equi-molar activity of [A] and [B], respectively.The value of Kas can be calculated using Eq. (7) as follows:

$$K_{as} = \frac{a_{AB}}{a_A a_B - a_A a_{AB} - a_B a_{AB} + a_{AB}^2} \quad (8)$$

It is now possible to compare the refractive index predicted using Eq. (6) with the experimental values, assuming any value of refractive index, nAB, in the hypothetical pure component AB. Different values of the sum of squares of deviations can be obtained by progressively increasing both the adjustable parameters Kas and nD,AB.

$$S = \sum (n_{obs} - n_{cal})^2 \quad (9)$$

The measured and computed refractive indexes are nobs and ncal, respectively.By modifying the values of Kas and nD,AB, the least value of S is attained. We set the value of nD,AB to be no lower than the least recorded refractive index and no substantially greater than the highest.

2.3Model Suggested by Glinski:

Glinski proposed that the equation assuming additivity with the volume fraction,φ of the components is similar to the improved version of Natta and Baccaredda model as follows:

$$n_{cal} = \frac{n_A n_B n_{AB}}{\varphi_A n_B n_{AB} + \varphi_B n_A n_{AB} + \varphi_{AB} n_A n_B} \quad (10)$$

where ncal is the theoretical refractive index of a binary liquid mixture, A, B are the volume percentages of component A and B, and nA, nB, and nAB are the refractive indices of component A, B, and AB, respectively. The numerical approach and determination of the association constant, Kas, is identical to that described above, with the benefit that, unlike the earlier method, no data on liquid mixture densities are required, except for those of pure components required to calculate the volume fractions. The concept had already been mentioned previously, and Reis et al. [18-21] and others.

3. Results and discussion:

The index of refraction values for 2-propenol, Benzyl alcohol, and 2-phenyl ethanol measured by Ching-Ta and Chein-Hsiun Tu were compared to those measured by Ching-Ta and Chein-Hsiun Tu and presented in Table1.

Table 1. Parameters of pure components

Component liquids	**T/ K**	**ρ/ gcm-3**		**nD**		**V/ cm3mol-1**
		Exp	Lit	Exp	Lit	
2-Propanol	298.15	0.78117	0.78123	1.37507	1.3752	76.5
	308.15	0.77253	—	1.37063	—	
	318.15	0.76352	—	1.36661	—	
Benzyl alcohol	298.15	1.0414	1.04127	1.53843	1.53837	
	308.15	1.0336	—	1.53421	—	
	318.15	1.02572	—	1.52994	—	
2-Phenylethanol	298.15	1.0162	—	1.53269	—	120.1
	308.15	1.00863	—	1.52852	—	
	318.15	1.00098	—	1.52427	—	

The deviation in the index of refraction was evaluated from Redlich-Kister equation as:

$$y = x_1(1 - x_1)\sum_{i=0}^{p} A_i\,(2x_1 - 1)^i \qquad (19)$$

where y denotes Δn, x1 denotes mole fraction, and Ai denotes coefficients. The values of coefficients Ai were calculated using the least squares approach in a multiple regression analysis, and are given in Table 2 along with the standard deviations between the experimental and fitted values of the corresponding function. Eq.as determines the standard deviation.

$$\sigma = \left[\sum_{i=1}^{m}\left(y_{exp_i} - y_{cal_i}\right)^2/(m-p)\right]^{1/2} \qquad (20)$$

where m is the number of experimental points and p is the number of adjustable parameters. For the case the σ values lie between (0.1- 0.6)×10-4 and the largest σ value (0.6×10-4) corresponds to 2-propanol+2-phenylethnolmixture at 298.15 K.

Table 2. Coefficient of Redlich- Kister coefficients and standard deviations,σ, for binary liquid mixtures

T/ K	A0	A1	A2	A3	σ×10-4
2-propanol+benzyl alcohol					
298.15	0.05768	0.00930	0.00354	-0.00069	0.1
308.15	0.05811	0.00881	0.00503	0.00110	0.2
318.15	0.05839	0.00839	0.00673	0.00251	0.5
2-propanol+2-phenylethnol					
298.15	0.07952	0.02025	0.00503	-0.00171	0.6
308.15	0.07976	0.02005	0.00797	-0.00113	0.3
318.15	0.07996	0.01985	0.01009	-0.00050	0.4
Benzyl alcohol+2-phenyl ethanol					
298.15	0.00413	-0.00043	0.00015	-0.00021	0.2
308.15	0.00459	-0.00037	0.00084	-0.00085	0.2
318.15	0.00491	-0.00023	0.00220	-0.00156	.25

Table 3. shows the McAllister three and four body interaction model coefficients as well as standard deviations for refractive indices. The coefficients a., b., and c have been determined using the least squares approach in Eqs. (15) and (18). For all of the systems, the four-body McAllister model is more consistently linked with the refractive index of the mixture than the three-body model.

Table 3. Coefficients of McAllister-3 and 4 Body interactions and their standard deviations (Δδ) forbinary liquid mixture

McAllister three Body Model				McAllister four Body Model			
T/K	A	B	Δδ	A	B	C	Δδ ×10-3
2-propanol+benzyl alcohol							
298.15	0.7271	1.0553	0.0012	1.4595	1.4928	1.5212	0.06
308.15	0.7250	1.0523	0.0012	1.4554	1.4883	1.5171	0.11
318.15	0.7228	1.0492	0.0014	1.2789	1.4020	1.5325	0.90
2-propanol+2-phenylethnol							
298.15	0.7646	1.0863	0.0024	1.4829	1.5011	1.5246	0.15
308.15	0.7623	1.0832	0.0026	1.4784	1.4966	1.5204	0.13
318.15	0.7600	1.0800	0.0027	1.4739	1.4921	1.5160	0.23
Benzyl alcohol+2-phenyl ethanol							
298.15	0.6756	0.9527	0.0001	1.5384	1.5381	1.5356	0.02
308.15	0.6737	0.9502	0.0002	1.5345	1.5338	1.5318	0.03
318.15	0.6779	0.9521	0.0018	1.5304	1.5294	1.5278	0.03

The absolute average percent deviation, %ΔnD, obtained from different models (associated and non-associated) were shown in Table 4 for comparison.

Table 4. Average absolute percent deviations of theoretical models for binary liquid mixtures

		Average Absolute % deviation					
T/K	Kas	nD, ab	nD, L-L	nD, RS	nD,Glinski	nD,McA3	nD,McA4
2-propanol+benzyl alcohol							
298.15	0.8	1.5382	0.0484	8.2583	8.5597	0.0786	0.0029
308.15	0.7	1.5382	0.0587	7.6849	7.6928	0.0857	0.0057
318.15	0.6	1.5279	0.0692	7.0561	6.7571	0.0935	5.5078
2-propanol+2-phenylethnol							
298.15	0.9	1.5324	0.0905	9.1089	8.9736	0.1557	0.0077
308.15	0.8	1.5282	0.0989	8.5022	8.2821	0.1680	0.0068
318.15	0.7	1.5235	0.1092	7.9748	7.3628	0.1776	0.0125
Benzyl alcohol+2-phenyl ethanol							
298.15	0.2	1.5365	0.1266	2.9771	2.9880	0.0008	0.0038
308.15	0.1	1.5299	0.1407	1.6484	1.5661	0.0032	0.0081
318.15	0.06	1.5299	0.1530	1.0499	0.9423	0.4238	0.0063

For the prediction of index of refraction and molar refractivity of binary mixes, Ramaswami and Abananthan's model was correlated. The model's fitting results were effectively utilized. The fitted parameters Kas and CAB (CAB is the refractive index and molar refractivity in the pure component AB) represent a hypothetical liquid containing only the association A-B. The equilibrium concentrations of species [A], [B], and [AB] will change as these parameters are simulated, and the refractive index and molar refractivity can be calculated. The sum of squares of deviations is calculated using the difference between experimental and theoretical values. It is

expected that three associates form in the solution rather than two (pure A, pure B and AB). In pure associate, the values of refractive index and molar refractivity can be treated as fitting with the value of Kas.
The following expression was used to calculate molar refractivity, Rm, from refractive index data:

$$R_m = [(n^2 - 1)/(n^2 + 2)]\, M/\rho \quad (21)$$

where M is the mean molecular weight of the mixture and ρ is the mixture density.

The molar refractivity deviation function shown in figures 1 & 2 has been calculated by the following expression:

$$\Delta R_m = R - \varphi_1 R_{m_1} - \varphi_2 R_{m_2} \quad (22)$$

where $\varphi_1$and φ_2 are volume fractions which is obtained by the relation as:

$$\varphi_i = \sum x_i V_i / \sum_{i=1}^{2} x_i V_i \quad (23)$$

There is no universal rule that specifies how to calculate a refractivity function. According to the Lorentz-Lorentz mixing laws, Konti et al [4] reported molar refractivity variances with volume fraction. Tables 4 and 5 contain data on mixtures.
When compared to the related models (L-L relation, McAllister three and four body), non-associated models (L-L relation, McAllister three and four body) produce good results for all binary systems at all temperatures, as shown in Table 5. At all temperatures, except in a few spots, the values of density refractive index and molar refractivity found from all models drop as the mole fraction increases. Except in a few areas reported in Table 5, as supplementary file, the results of molar refractivity obtained from Eq. 13 for the complete systems exhibit a regular pattern.as supplementary file.
Tables show the negative and positive values of deviation in molar refractivity, Rm, for all of the mixes. Because hydrogen bonding is more temperature dependent than columbic interactions, this phenomenon can be explained. In general, the maximum variance for all models occurs at a mole fraction of 0.4-0.6. When using the L-L mixing rule, the value of Rm is less negative, while when using the RS model, it is more negative. Similarly, the L-L mixing rule yields fewer positive deviations while the Glinski model yields more. In general, the position of the hydroxyl group on the alcohol chain is indicated by the more positive or negative value of Rm. The trend in all of the Figs is nearly same. For all systems, molar refraction increases as molecule weight increases. As shown in Table 5 as a supplemental file, density and refractive index are affected by molecular weight and the composition of the solution, and values drop as temperature rises.

4. Conclusions:

We give the theoretical conclusions of deviation in molar refractivity, Rm, and index of refraction, n, for three binary systems based on Ching-Ta et al's experimental data. Associated and non-associated models were used to examine the measured data. We chose liquids with interacting properties but a high level of technological significance in the chemical industry for this aim. The negative and positive values of Rm can be explained by the fact that hydrogen bonding breaks at a higher temperature than columbic interactions. In general, the position of the hydroxyl group on the alcohol chain is indicated by the more positive or negative value of Rm. The density and refractive index of a solution are determined by the molecular weight and nature of the solution, and their values drop as the temperature rises. At all temperatures, except in a few spots, the values of density, refractive index, and molar refractivity drop as the mole fraction increases. When compared to experimental data, the Lorentz-Lorentz mixing rule appears to produce better results than alternative models.

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