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Computational Approach of Molar Refraction, Molecular Radius and Internal Pressure of a Binary Mixture – Molecular Interaction Studies

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Abstract

Refractive indices and molar volume of binary liquid mixture of 1,4-dioxane with 1-butanol were measured over the entire composition range at T= (298.15, 303.15, 308.15, 313.15 & 318) K using Anton Paar and Abbemat Refractometer. Basing empirical formulae and the measured data were utilised to evaluate the molar refraction (Rm), molecular radii (r), internal pressure (πi) along with their excess parameters. The computed results of 'RmE, rE and πiE' were fitted to the Redlich—Kister polynomial equation and focused on the molecular interactions present in the mixture.

Keywords: Refractive Indices, Molar Refraction, Molecular Radii, Internal Pressure, 1,4-Dioxane, 1-Butanol, Binary Mixtures

Introduction

The molecular radii (r) are one of the important parameters of pure liquids and liquid mixtures, which reflect their structural features. In recent years, several attempts have been made to predict theoretically the values of molecular radii of liquid and liquid mixtures. Complex formation/ interactions in liquid mixtures have been extensively studied using optical and ultrasonic technique by many workers (Gonzalez, & Dominguez, 2004; Jiangtao, 2005; Kadam, 2006). The formation of hydrogen bond in solutions and its effect on the physical properties of the mixtures have received much attention. Hydrogen bonding plays an important role in fundamental sciences and in industrial applications. Although many experimental and theoretical studies have been directed towards understanding of hydrogen bonding, it remains an area of active research. Knowledge of physico-chemical properties of liquid mixtures formed by two or more components associated through hydrogen bonds is important from theoretical and process design aspects. Further, the investigation on the possible changes in these properties of mixtures has been found to be an excellent qualitative and quantitative way to elicit the information about molecular structure and intermolecular forces present in the liquid mixtures.

Refractive index is one of the most important properties of liquid. It is an important additive property of the structural arrangement of atom in molecule. Ubarhande (2011) measured refractive indices of binary liquid mixtures and 1,3 diaryl carbamides in different percentage of binary liquid mixture such as acetone-water, dioxane-water & DMSO-water at 27± 0.1^0C were measured by Abbes' refractrometer. The data obtained by them was utilised to calculate molar refraction & polarizability constant and reported the attractive force may arise from temporary dipole formation in solvent which may produce weak inter molar force like dispersion force.

Pandey and Dey (2004); Sonar (2010); Pawar (2012); and Prajapati (2012) used several empirical relations based on acoustic methods to calculate the molecular radii of pure liquids. Molecular radii (r) of the pure liquids or binary mixtures can be estimated using refractive index data (n) and molar volume (V_m), it is given as;

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$$r = \left[\frac{3}{4\pi N} V_m \frac{n^2-1}{n^2+2}\right]^{1/3} \quad (1)$$

The refractive index of a material is defined as the ratio c/v, where 'v' is the speed of light in the material and 'c' the speed of light in vacuum. This dimensionless optical property is very sensitive to changes in the molecular association of pure liquids, solutions, and mixtures. From the measured values of refractive indices molar refraction (R_m), the actual volume of the mixture is calculated using the relation,

$$R_m = \left[\frac{n^2-1}{n^2+2}\right] V_m \quad (2)$$

Using Molar volume (V_m) and molecular radii (r) we can predict internal pressure (π_i) of the mixture on the basis of Buchler-Hirschfelder Curties equation of state (Hirschfelder, 1965) as,

$$\pi_i = \frac{2^{\frac{1}{6}} RT}{2^{\frac{1}{6}} V_m - 2rN^{\frac{1}{3}} V_m^{2/3}} \quad (3)$$

Further, the excess parameters were fitted to Redlich – Kister polynomial equation to estimate the adjustable parameters.

$$Y^E = x_1 x_2 \sum_{i=0}^{n} a_i (1-2x)^i \quad (4)$$

using least-squares regression method, the (a_i) coefficients are obtained by fitting above equation to the experimental values. The optimum number of coefficients is ascertained from an examination of the variation in standard deviation (σ)

$$\sigma(Y) = \left[\frac{\sum (Y_{expt} - Y_{calc})^2}{N-n}\right]^{1/2} \quad (5)$$

Table 1: Refractive Indices (n) and Molar Volume (V_m) Values at Various Mole Fractions of 1,4-Dioxane in 1,4-Dioxane + 1-Butanol Mixtures at Different Temperatures

X_1	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
n (Refractive indices)					
0.0000	1.3974	1.3954	1.3934	1.3914	1.3893
0.1149	1.3990	1.3970	1.3948	1.3927	1.3905
0.2123	1.4008	1.3987	1.3963	1.3941	1.3918
0.3037	1.4025	1.4003	1.3981	1.3958	1.3934
0.4068	1.4046	1.4024	1.4001	1.3976	1.3953
0.5112	1.4069	1.4045	1.4021	1.3996	1.3972
0.6297	1.4096	1.4070	1.4046	1.4023	1.3998
0.7066	1.4114	1.4088	1.4063	1.4041	1.4014
0.7993	1.4139	1.4115	1.4090	1.4065	1.4039
0.9065	1.4168	1.4144	1.4119	1.4092	1.4069
1.0000	1.4194	1.4170	1.4145	1.4121	1.4097
V_m*10^{-4} m^{3}mol^{-1} (Molar volume)					
0.0000	1.0924	1.0977	1.1030	1.1084	1.1140
0.1149	1.0447	1.0513	1.0579	1.0623	1.0671
0.2123	1.0047	1.0097	1.0149	1.0201	1.0254
0.3037	0.9671	0.9721	0.9771	0.9822	0.9874
0.4068	0.9264	0.9312	0.9361	0.9411	0.9461
0.5112	0.8867	0.8913	0.8958	0.9010	0.9056
0.6297	0.8436	0.8483	0.8530	0.8575	0.8616
0.7066	0.8164	0.8214	0.8252	0.8298	0.8336
0.7993	0.7852	0.7893	0.7927	0.7969	0.8013
0.9065	0.7509	0.7551	0.7584	0.7621	0.7669
1.0000	0.7219	0.7258	0.7299	0.7326	0.7382

where N is the number of data points and n is the degree of fitting.

Experimental

The experimental liquids 1,4-dioxane and 1-butanol with mass fraction purities >0.998 were purchased from Sigma Aldrich chemical company, the chemical mixtures in eleven mole fractions were kept in airtight glass bottles in an isothermal mode. The measurements were performed using the sound analyzer incorporated in the using Anton Paar devices DSA 5000M, Abbemat Refractometer RXA 170 the ultrasonic velocity, density and refractive index are measured at five different temperatures. The details of the experimental work, data related to ultrasonic velocity, density and refractive index, derived parameters of the mixture are reported in detail in their earlier papers of the author (Kumar & Srinivasu, 2013, 2014). The refractive indices, molar volume of the mixture measured at five temperatures are reported in Table 1.

Using the data given in Table 1 and empirical formulae with C-programming molar refraction, molecular radii and internal pressure are estimated at five temporaries.

The uniqueness of C-language in its simplicity, compactness, versatility etc., is effectively utilised here, in writing an efficient program for the computation of the parameters and their excess values with standard symbols of a binary liquid mixture (for eleven mole fractions).

```
#include<stdio.h>

#include<math.h>

main()

{

int i;

float x1[11],n[11],Vm[11],Rm[11],r[11],πi[11];

float T,r1,r2,r3, π1, π2, π3, π4;

float EP_n[11],EP_Rm[11],EP_r[11],EP_πi[11];

clrscr();

printf("\n Enter T value:");

scanf("%f",&T);

printf("\n Enter x1 values:");

for(i=1;i<=11;i++)

scanf("%f",&x1[i]);

printf("\n Enter n values:");

for(i=1;i<=11;i++)

scanf("%f",&n[i]);

printf("\n Enter Vm values:");

for(i=1;i<=11;i++)

scanf("%f",&Vm[i]);

for(i=1;i<=11;i++)

{

Rm[i]=(((n[i]*n[i])-1)/((n[i]*n[i])+2)*Vm[i])*pow(10,2);

r1=(3.978357734*pow(10,-25));

r2=(Vm[i]*((n[i]*n[i])-1)/((n[i]*n[i])+2));

r3=r1*r2;

r[i]=pow(r3,0.333);

π1=(pow(2,0.1666)*8.314*T);

π2=(((pow(2,0.1666)*Vm[i])-(2*r[i]*(6*pow(10,23))))*(
pow(Vm[i],0.6666)));

πi[i]=((π1/π2)*pow(10,-4));

}

printf("\n x1[i] \t n[i] \t Vm[i] \t Rm[i] \t r[i] \t πi[i]");

printf("\n----------------------------------------------------");

for(i=1;i<=11;i++)

printf("\n %.4f %.4f %.4f %.4f %.4f %.4e %.4f %.4e",x1
[i],n[i],Vm[i],Rm[i],r[i],πi[i]);

for(i=1;i<=11;i++)

{

EP_n[i]=n[i]-(x1[i]*n[11]+((1-x1[i])*n[1]));
```

1. In according to: Eshlaghy and Farokhi (2011, pp. 7 and 8).

```
EP_Rm[i]=Rm[i]-(x1[i]*Rm[11]+((1-x1[i])*Rm[1]));

EP_r[i]=r[i]-(x1[i]*r[11]+((1-x1[i])*r[1]));

EP_πi[i]=πi[i]-(x1[i]*πi[11]+((1-x1[i])*πi[1]));

}

printf("\nEP_n[i] EP_Rm[i] EP_r[i] EP_πi[i]");

printf("\n----------------------------------------------");

for(i=1;i<=11;i++)

printf("\n %.4e %.4e %.4e %.4e %.4e %.4e",EP_n[i],EP_Rm[i],EP_r[i],EP_πi[i]);

getch();

}
```

With the help of above program the author reports Table 2 (shows molar refraction 'R_m', molecular radii 'r' and internal pressure 'π_i') and Table 3 (excess molar refraction 'R_m^E', excess molecular radii 'r^E', and excess internal pressure 'π_i^E') at five different temperatures T=(298.15, 303.15, 308.15, 313.15 and 318.15 K).

Results and Discussion

On close perusal of Table 2 it is noticed that at all five temperatures as mole fraction of 1,4-dioxane increases, for 1,4-dioxane with 1-butanol, 'R_m, r' values decreases and 'π_i' values increases.

Table 3 revels that excess molar refraction (R_m^E), excess molecular radii (r^E) and excess internal pressure (π_i^E) for the binary mixtures shows smaller negative values. These excess functions give an idea about the extent to which the given liquid mixtures deviate from ideality and they are important in understanding the intermolecular interactions and nature of molecular campaigning in hetero molecules.

All the evaluated excess parameters were fitted to Redlich–Kister polynomial, and the corresponding graphs are shown in Figs. 1, 2 and 3 respectively.

Molar refraction is a measure of the total polarizability of a mole of a substance and is dependent on the temperature, the index of refraction and the pressure. The molar refraction (R_m) is related to both refractive index

Table 2: Molar Refraction (R_m), Molecular Radius (r) and Internal Pressure (π_i) Values at Various Mole Fractions of 1,4-Dioxane in 1,4-Dioxane + 1-Butanol Mixtures at Different Temperatures

x_1	$10^{-3}\ R_m\ m^3mol^{-1}$	$10^{-9}\ r\ m$	$10^4\ \pi_i\ pa$	$10^{-3}\ R_m\ m^3mol^{-1}$	$10^{-9}\ r\ m$	$10^4\ \pi_i\ pa$
	298.15 K			*313.15 K*		
0.0000	26.3275	4.7138	0.7270	26.3562	4.7155	0.7451
0.1149	25.2703	4.6498	0.7621	25.3354	4.6538	0.7792
0.2123	24.4020	4.5960	0.7949	24.4051	4.5962	0.8132
0.3037	23.5770	4.5436	0.8280	23.5879	4.5443	0.8469
0.4068	22.6846	4.4855	0.8674	22.6931	4.4861	0.8866
0.5112	21.8229	4.4280	0.9096	21.8259	4.4282	0.9291
0.6297	20.8820	4.3634	0.9602	20.8940	4.3642	0.9806
0.7066	20.2891	4.3217	0.9953	20.2965	4.3222	1.0162
0.7993	19.6179	4.2735	1.0389	19.5957	4.2719	1.0624
0.9065	18.8763	4.2190	1.0915	18.8515	4.2171	1.1157
1.0000	18.2434	4.1713	1.1401	18.2329	4.1705	1.1663
303.15 K				**318.15 K**		
0.0000	26.3399	4.7145	0.7332	26.3663	4.7161	0.7506
0.1149	25.3178	4.6528	0.7676	25.3257	4.6532	0.7852
0.2123	24.4051	4.5962	0.8013	24.4089	4.5964	0.8189
0.3037	23.5802	4.5438	0.8346	23.5897	4.5444	0.8527
0.4068	22.6946	4.4862	0.8743	22.6972	4.4863	0.8925
0.5112	21.8202	4.4278	0.9164	21.8192	4.4277	0.9355

x_1	$10^{-3} R_m\ m^3 mol^{-1}$	$10^{-9} r\ m$	$10^4 \pi_i\ pa$	$10^{-3} R_m\ m^3 mol^{-1}$	$10^{-9} r\ m$	$10^4 \pi_i\ pa$
	298.15 K			*313.15 K*		
0.6297	20.8825	4.3634	0.9669	20.8777	4.3631	0.9874
0.7066	20.3008	4.3225	1.0015	20.2723	4.3205	1.0233
0.7993	19.6163	4.2734	1.0468	19.5915	4.2716	1.0689
0.9065	18.8841	4.2196	1.0993	18.8729	4.2187	1.1223
1.0000	18.2505	4.1718	1.1484	18.2774	4.1739	1.1712
308.15 K						
0.0000	26.3498	4.7151	0.7393			
0.1149	25.3524	4.6549	0.7726			
0.2123	24.4033	4.5960	0.8073			
0.3037	23.5848	4.5441	0.8409			
0.4068	22.7005	4.4866	0.8807			
0.5112	21.8164	4.4275	0.9234			
0.6297	20.8883	4.3638	0.9736			
0.7066	20.2851	4.3214	1.0092			
0.7993	19.5975	4.2720	1.0552			
0.9065	18.8643	4.2181	1.1081			
1.0000	18.2586	4.1724	1.1563			

Table 3: Excess Molar Refraction (R_m^E), Molecular Radius (r^E) and Internal Pressure (π_i^E) Values at Various Mole Fractions of 1,4-Dioxane in 1,4-Dioxane + 1-Butanol Mixtures at Different Temperatures

x_1	$10^{-3} R_m^E\ m^3 mol^{-1}$	$10^{-9} r^E\ m$	$10^4 \pi_i^E\ pa$	$10^{-3} R_m^E\ m^3 mol^{-1}$	$10^{-9} r^E\ m$	$10^4 \pi_i^E\ pa$
	298.15 K			*313.15 K*		
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1149	-0.1232	-0.0013	-0.0124	-0.0902	0.0008	-0.0144
0.2123	-0.2183	-0.0033	-0.0196	-0.2186	-0.0031	-0.0212
0.3037	-0.2915	-0.0053	-0.0244	-0.3086	-0.0062	-0.0260
0.4068	-0.3491	-0.0073	-0.0278	-0.3596	-0.0078	-0.0299
0.5112	-0.3752	-0.0087	-0.0287	-0.3700	-0.0082	-0.0315
0.6297	-0.3597	-0.0091	-0.0267	-0.3513	-0.0084	-0.0295
0.7066	-0.3218	-0.0085	-0.0237	-0.3229	-0.0084	-0.0261
0.7993	-0.2469	-0.0066	-0.0184	-0.2626	-0.0076	-0.0200
0.9065	-0.1252	-0.0031	-0.0099	-0.1432	-0.0045	-0.0108
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
303.15 K				**318.15 K**		
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1149	-0.0939	0.0005	-0.0135	-0.1121	-0.0006	-0.0139
0.2123	-0.2148	-0.0031	-0.0201	-0.2366	-0.0044	-0.0209
0.3037	-0.3028	-0.0060	-0.0245	-0.3235	-0.0073	-0.0257
0.4068	-0.3596	-0.0079	-0.0280	-0.3801	-0.0093	-0.0292
0.5112	-0.3788	-0.0089	-0.0293	-0.4049	-0.0108	-0.0303
0.6297	-0.3628	-0.0093	-0.0277	-0.4022	-0.0121	-0.0279
0.7066	-0.3284	-0.0089	-0.0246	-0.3767	-0.0124	-0.0243
0.7993	-0.2544	-0.0071	-0.0190	-0.3072	-0.0109	-0.0183

x_1	$10^{-3} R_m^E$ m^3mol^{-1}	$10^{-9} r^E$ m	$10^4 \pi_i^E$ pa	$10^{-3} R_m^E$ m^3mol^{-1}	$10^{-9} r^E$ m	$10^4 \pi_i^E$ pa
	298.15 K			313.15 K		
0.9065	-0.1239	-0.0031	-0.0100	-0.1625	-0.0060	-0.0094
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
308.15 K						
0.0000	0.0000	0.0000	0.0000			
0.1149	-0.0741	0.0017	-0.0146			
0.2123	-0.2155	-0.0031	-0.0207			
0.3037	-0.3139	-0.0067	-0.0247			
0.4068	-0.3683	-0.0085	-0.0282			
0.5112	-0.3825	-0.0092	-0.0297			
0.6297	-0.3722	-0.0100	-0.0278			
0.7066	-0.3481	-0.0103	-0.0243			
0.7993	-0.2852	-0.0093	-0.0180			
0.9065	-0.1500	-0.0051	-0.0089			
1.0000	0.0000	0.0000	0.0000			

and molecular properties of compound. The 'R_m' value of compound can be often predicated by structural feature of molecule. Each constituent atom or group's contribution portion to final 'R_m' value in connection with additive constituent properties. Magnitude and sign of excess molar refraction give strength of molecular interaction.

Generally, the 'R_m^E' represents the electronic perturbation due to orbital mixing of two components and gives information regarding the strength of interaction in mixture and is sensitive function of wavelength, temperature and mixture composition. That means more the positive deviation of 'R_m^E' suggests more electronic perturbation in the mixture and concludes the dipole–dipole and donor–acceptor interaction between unlike molecules of the mixture. But the 'R_m^E' related plot of the mixture shows that 'R_m^E' values are of less magnitude of negative values indicates the presence of not so strong interactions. Further, from equations 1,2 it is understood that 'r' and 'R_m' are alike in showing the results. This is clearly supported from Tables 2, 3 and Figs. 1, 2.

Internal energy is simply the totality of all forms of kinetic and potential energy of a system. The study of liquid mixtures internal pressure gives reliable information regarding nature and strength of forces existing in a

Fig. 1: Excess molar Refraction of the Binary System {x_1 1,4-Dioxnae + (1−x_1) 1-Butanol }at: ♦, 298.15 K; ■, 303.15 K; ▲, 308.15 K; x, 313.15 K, *, 318.15 K; Solid line; Redlich–Kister Equation.

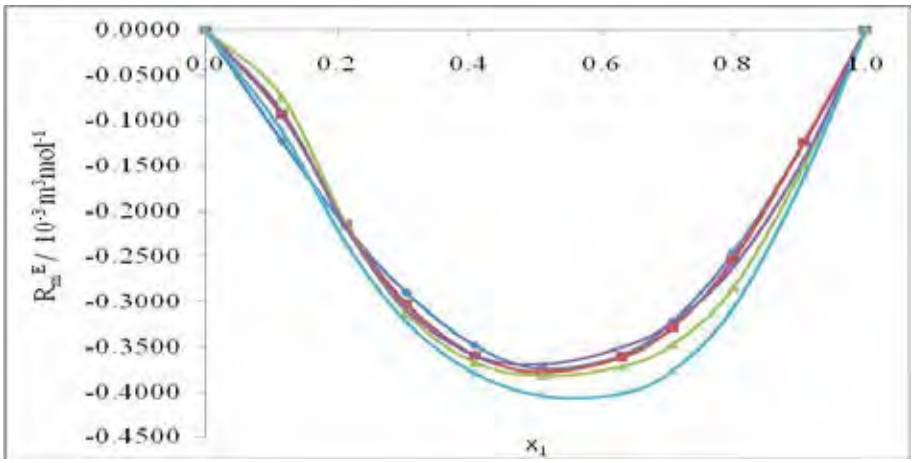


Fig. 2: Excess Molecular Radii of the Binary System {x_1 1,4-Dioxnae + (1−x_1) 1-Butanol }at: ♦, 298.15 K; ■, 303.15 K; ▲, 308.15 K; x, 313.15 K, *, 318.15 K; Solid line; Redlich–Kister Equation.

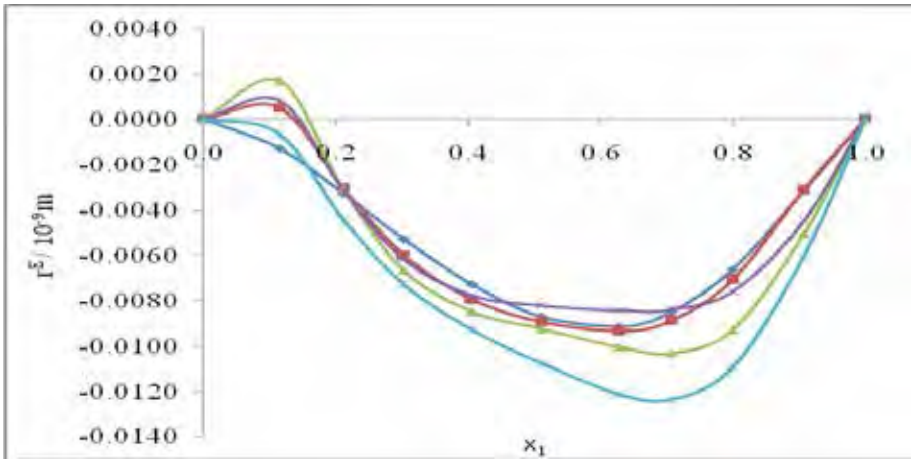
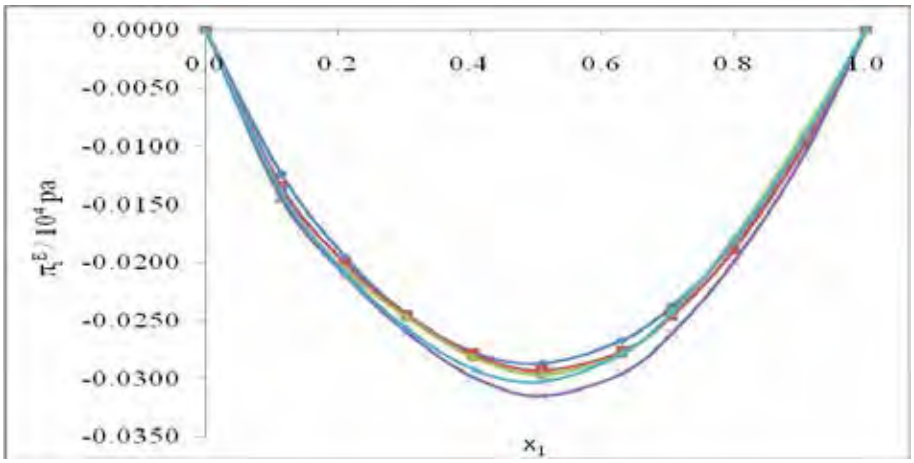


Fig. 3: Excess Internal Pressure of the Binary System {x_1 1,4-Dioxnae + (1−x_1) 1-Butanol }at: ♦, 298.15 K; ■, 303.15 K; ▲, 308.15 K; x, 313.15 K, *, 318.15 K; Solid line; Redlich–Kister Equation.



mixture. When two molecules are under sort of attraction, like hydrogen bonding, the internal pressure value increases. In fact internal pressure is a border concept and is a measure of totality of forces dispersion, ionic, dipolar interaction that contribute to overall cohesion of the liquid system. Bhatia and Bhatia (2009) reported that the positive deviations in 'π_i^E' indicate attractive forces are greater than the repulsive interactions while the small negative deviations indicates loosing cohesion of molecules in the system implying weak intermolecular interactions. The present investigation for 1,4-dioxane with 1-butanol shows the excess internal pressure are negative at all five temperatures. The same is found in Fig. 3. The negative values of excess internal pressure indicate the presence of weak dipolar forces are operating between unlike molecules of the mixture.

Conclusion

From the data of refractive index & molar volume (V_m), we have estimated molar refraction (R_m), molecular radii (r) and internal pressure (π_i) with empirical formulae. The parameters and their excess values are computed, the results of excess functions are fitted to the Redlich–Kister equation. Basing on the excess parameters study it is observed that not strong interactions are present in 1,4-dioxane + 1-butanol binary mixture.

List of symbols:

U - Ultrasonic velocity

ρ - Density

n - Refractive indices

R_m - Molar refraction

r - Molecular radius

π_i - Internal pressure

R_m^E - Excess molar refraction

r^E - Excess molecular radius

π_i^E - Excess internal pressure

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