

Surface Properties of Benzyl alcohol + 2-Phenyl ethanol Binary Mixture at three different temperatures

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Abstract:

Theoretical results for Surface tension and excess volume were studied for the binary system formed by Benzyl alcohol + 2-Phenyl ethanol at 298.15, 308.15 and 318.15 K and atmospheric pressure over the concentration range 0.05-0.95, from the experimental data of Ching-Ta and Chein-Hsiun Tu. Various theoretical models of liquid state were utilized to study the association properties of strong interacting liquids. Deviations in the surface tension were evaluated and fitted to the Redlich-Kister polynomial to derive the binary coefficients and standard errors. Furthermore, McAllister multi body interaction model based on Eyring's theory of absolute reaction rates, has been applied. For liquid mixtures, the free energy of activation is additive, based on the proportions of the different components of the mixture and interactions of like and unlike molecules. Conclusively, the association behavior of the liquids was correlated with molecular interactions using the different liquid state models which were compared and tested for different systems showing that the McAllister multi body interaction model yields good results as compared to associated models.

Keywords: Surface tension, Excess volume, Binary, Association properties, Liquid models

Introduction:

Surface tension is an important property in many scientific and technological areas such as liquid-liquid extraction, gas absorption, distillation, condensation, material sciences, process simulation, molecular dynamics [1,2] ect. and in industries [3] such as paints, detergents, agrochemicals and petroleum. Also, it is a parameter that describes the thermodynamic state and contains important information regarding the internal structure of a liquid interface. Apart from theoretical interest, it describes the behavior of a vapor-liquid interface, such as enrichment of one component in a liquid surface that is used in modeling a distillation process. Numerous studies [4-7] on surface tension have been investigated in past but their systematic theoretical and experimental investigations of vapor-liquid interfaces for the prediction of association behavior are rare, particularly in a wide temperature and concentration range. High quality of experimental data of surface tensions forms the basis for a successful modeling and for theoretical calculations of surface properties [8, 9]. The paper is concerned with the mixing properties for two types of flavor alcohols, such as benzyl

alcohol mixed with 2-phenylethanol. These alcohols are vitally related to our daily lives. Benzyl alcohol is used in perfumery and is widely used in microscopy as the embedding material [10] and is also important as a solvent for gelatin and in pharmaceutical applications as an anti-microbial agent [11]. 2-Phenylethanol is used in artificial essence and as a base solvent for some flavor compounds. The main objective of this work was to study the behavior and molecular interactions involved in the liquid mixtures, by utilizing various theoretical models. Here, we present the theoretical results of surface tension and excess volume from the experimental work of Ching-Ta et al [12] for the binary liquid mixtures formed by Benzyl alcohol+2-Phenyl ethanol at 298.15, 308.15 and 318.15 K and atmospheric pressure over the concentration range 0.05-0.95. To compare the merits of various models, the data were analyzed using the Ramaswamy and Anbanathan (RA) model [13], a model suggested by Glinski [14] and the statistical model of Flory [15-17]. The first two of these models assume association of the components of the mixture, and include the association constant as an adjustable parameter. By contrast, the Flory model assumes the components do not associate (non-association), and that the behavior of each of the liquids in the mixture is simply additive when determining the overall properties. In the present study, we used liquids that usually show strong interactions. Changes in the surface tension ($\Delta\sigma$) were evaluated and fitted to the Redlich-Kister polynomial [18] to derive the binary coefficients and standard errors. An attempt was made to correlate the experimental data with the McAllister multi body interaction model [19], based on Eyring's theory of absolute reaction rates.

Modeling:

Flory model (Surface Tension):

The original cell model of Prigogine [20] for spherical chain molecules uses a dependence of the configurational energy on volume equivalent to the Lennard-Jones (6, 12) energy-distance relation i.e.

$$U(v) = -2v^{-6} + v^{-12} \quad (1)$$

More generally for (m, n) potential,

$$\tilde{U}(\tilde{v}) = \frac{(-n\tilde{v}^{-m/3} + m\tilde{v}^{-n/3})}{(n-m)} \quad (2)$$

This leads to the following equation of state

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = (1 - b\tilde{v}^{-1/3})^{-1} + \frac{mn}{3(n-m)} (\tilde{v}^{-n/3} - \tilde{v}^{-m/3}) \quad (3)$$

where b is a packing factor and equals to $(m/n)^{1/(n-m)}$

Flory and collaborators [15-17] used the cell partition function of Hirschfelder and Eyring and a simple Van der Waals

energy- volume relation, $\tilde{U} = -\tilde{v}^{-1}$, by putting $m=3, n \rightarrow \infty$ so that the Flory equations for the mixing functions may be obtained from the general corresponding state equations by making this particular choice of (m, n) . Patterson et al [16] have drawn attention to the close connection between the Flory theory and corresponding state theory of Prigogine [20] employing a simple cell model of the liquid state. The equation of state for the materials conforming to the principle of corresponding state that can be expressed in a universal form through the use of suitable characteristic and reduction parameters for the pressure, volume and temperature respectively.

In order to extend corresponding state theory to deal with the surface tension, Patterson and Rastogi [16] used the reduction parameters as,

$$\sigma^* = k^{1/3} P^{*2/3} T^{*1/3} \quad (4)$$

called the characteristic surface tension of the liquid. Here k is the Boltzmann constant. A segment experiences an increase in the configurational energy equal to $-M\tilde{U}(\tilde{v}_s)$ due to the loss of a fraction, M , of its nearest neighbors at the surface while moving from the bulk phase to the surface phase. It's most suitable value ranges from 0.25 to 0.29. In the present case the value of M is taken as 0.29 throughout the calculation.

Thus the Surface tension of liquid mixture is given by the

expression as;

$$\sigma = \sigma^* \tilde{\sigma}(\tilde{v}) \quad (5)$$

Excess volume:

The excess volume of binary liquid mixture can be obtained by the equation as;

$$\tilde{v} - \tilde{v}_0 = v^E = \frac{v^E}{x_1 v_1^* + x_2 v_2^*} \quad (6)$$

where \tilde{v}_0 is the ideal reduce volume and it is given as;

$$\tilde{v}_0 = \psi_1 \tilde{v}_1 + \psi_2 \tilde{v}_2 \quad (7)$$

substitution of eq.(7) in eq.(6) directly gives the excess volume of binary system with slight rearrangement which can be represented as

$$v^E = [(x_1 v_1^* + x_2 v_2^*) [\tilde{v} - (\psi_1 \tilde{v}_1 + \psi_2 \tilde{v}_2)]] \quad (8)$$

where v^E is the excess molar volume and \tilde{v} is the reduced molar volume of the binary liquid mixtures, assuming that the volume reduction parameters of the binary mixtures to be linear in mole fraction.

where v is the molar volume of the liquid mixture and represented by ρ is the density of the mixture. The above mentioned equation has been utilized for the computation of excess volume of binary liquid mixtures.

RA Model:

Ramswamy and Anbananthan [13] proposed the model based on the assumption of linearity of acoustic impedance with the mole fraction of components. Further, we assumed that any equilibrium physical property such as viscosity, refractive index, surface tension etc. based on linearity can be predicted well.

Assuming that when solute is added to solvent the molecules interact according to the equilibrium as:



and the association constant K_{as} can be defined as;

$$K_{as} = \frac{[AB]}{[A][B]} \quad (10)$$

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

By applying the condition of linearity in surface tension with composition, we get;

$$\sigma_{obs} = x_A \sigma_A + x_{AB} \sigma_{AB} \quad (11)$$

where x_A, x_{AB}, σ_A and σ_{AB} and σ_{obs} are the mole fraction of A, mole fraction of associate AB, surface tension of A, surface tension of associate AB and observed surface tension respectively. The equilibrium reaction in the eq (11) is not complete by definition as there are molecules of non-associated component present in the liquid mixture prevailing in the high solute content. Considering the non-associated component present in the liquid mixture eq takes the form,

$$\sigma_{obs} = [x_A \sigma_A + x_B \sigma_B + x_{AB} \sigma_{AB}] \quad (12)$$

where x_B and σ_B are the mole fraction of B and surface tension of B (non-associated component).

Now, assuming any value of surface tension in the hypothetical pure component AB, σ_{AB} , it is possible to compare the surface tension calculated using eq. (12) with the experimental values. On changing both the adjustable parameters K_{as} and σ_{AB} gradually, one can get different values of the sum of squares of deviations,

$$S = \sum (\sigma_{obs} - \sigma_{cal})^2 \quad (13)$$

where σ_{obs} and σ_{cal} are the observed and calculated surface tension respectively. The minimum value of S can be obtained theoretically by a pair of the fitted parameters, but we found

that for some K_{as} and σ_{AB} , the value of S is high and changes rapidly while for others, it is low and changes slowly when the fitted parameters are being changed. In such cases, the value of σ_{AB} should not be much lower than the lowest observed acoustic velocity of the system or much higher than the highest one. Quantitatively, it should be reasonable to accept the pair of adjustable parameters K_{as} and σ_{AB} which has the physical sense and reproduces the experimental physical property satisfactorily.

Model Suggested by Glinski:

On inspecting the results obtained from RA model, Glinski suggested the equation assuming additivity with the volume fraction, ϕ of the components, the refined version of Natta and Baccaredda model [21] as,

$$\sigma_{cal} = \frac{\sigma_A \sigma_B \sigma_{AB}}{\phi_A \sigma_B \sigma_{AB} + \phi_B \sigma_A \sigma_{AB} + \phi_{AB} \sigma_A \sigma_B} \quad (14)$$

where σ_{cal} is the theoretical surface tension of binary liquid mixture, ϕ_A , ϕ_B are the volume fractions of component A and B and σ_A , σ_B and σ_{AB} are the surface tension of components A, B and AB. The numerical procedure and determination of association constant, K_{as} , was similar to that described before and the advantage of this method as compared with the earlier one was that the data on densities of liquid mixture are not necessary except those of pure components needed to calculate the volume fractions. In this context the importance of models assuming associated liquids already mentioned and was further developed and elaborated by Reis et al [22].

McAllister – three body model:

McAllister considered a number of different three bodied planar encounters in the study of the viscosity of a mixture of molecules type (1) and (2). He proposed that the total free energy of activation will be dependent on the free energy of activation (ΔG_i , ΔG_{ij} or Δs_{ijk}) of individual interactions and their fraction of total occurrences (x_i^3 , $x_i^2 x_j$, x_j^2 , $x_i x_j^2$

or $x_i x_j x_k$). Now applying Eyring eq. for each set of interactions (i.e.111,121,211, 112; 212, 122, 221; and 222) and then taking logarithms of equations so obtained to eliminate free energy terms, following equation is obtained

$$\begin{aligned} \ln \sigma &= x_1^3 \ln \sigma_1 + 3x_1^2 x_2 \ln \sigma_{12} + 3x_1 x_2^2 \ln \sigma_{21} \\ &+ x_2^3 \ln \sigma_2 - \ln[x_1 + x_2 M_2 / M_1] + 3x_1^2 x_2 \ln[(2 + M_2 / M_1) / 3] \\ &+ 3x_1 x_2^2 \ln[(1 + 2M_2 / M_1) / 3] + x_2^3 \ln[M_2 / M_1] \end{aligned} \quad (15)$$

where $M_{12} = \frac{2M_1 + M_2}{3}$ and $M_{21} = \frac{M_1 + 2M_2}{3}$ (16)

McAllister –four body model:

If there is a much difference in size of two molecules, then a four body model approaches nearly a 3-dimensional treatment. Again considering different interactions and their fraction of total occurrences, energy of activation may be written as sum of energy of activations of various interactions as;

$$\begin{aligned} \ln \sigma_{mix} &= x_1^4 \ln \sigma_1 + 4x_1^3 x_2 \ln \sigma_{1112} + 6x_1^2 x_2^2 \ln \sigma_{1122} \\ &+ 4x_1 x_2^3 \ln \sigma_{222} + x_2^4 \ln \sigma_2 - \ln(x_1 + x_2 M_2 / M_1) \\ &+ 4x_1^3 x_2 \ln[(3 + M_2 / M_1) / 4] + 6x_1^2 x_2^2 \ln[(1 + M_2 / M_1) / 2] \\ &+ 4x_1 x_2^3 \ln[(1 + 3M_2 / M_1) / 4] + x_2^4 \ln(M_2 / M_1) \end{aligned} \quad (17)$$

where σ , x_1 , σ_1 , M_1 , x_2 , σ_2 and M_2 are the surface tension of mixture, mole fraction, surface tension and molecular weight of pure component 1 and 2 respectively. McAllister coefficients are adjustable parameters that are characteristic of the system.

Results & Discussion:

The associated models (RA and Glinski) which assume linearity with the amount of substance fraction of components, were used to predict the surface tension of mixture components that was corrected [14] and tested to predict the behavior of each mixture with association between the components. The calculations were performed using a computer program and the parameters were adjusted either automatically or manually. The association constant (K_{as}) and $\sigma_{A,B}$ were used as the fitted parameters, where $\sigma_{A,B}$ is the surface tension in a hypothetical pure liquid with only the species AB formed by association of the components A and B. When the parameters are changed, the equilibrium concentrations of the species [A], [B], and [AB] will change and this could affect the surface tension. The differences between experimental and theoretical surface tension values were used to obtain sum of squares for the deviation. It was assumed that three species (A, B, and AB) were present in solution instead of only two (A and B) because of formation of the AB species by association after mixing. Comparison of measured density and surface tension of pure solvents with literature value at 298.15K were presented in Table 1.

Table 1 Comparison of density and Surface Tension with literature data for pure components at 298.15, 308.15, and 318.15 K

Component	T/K	Density ρ / (g/cc)		Surface Tension σ / mN.m ⁻¹	
		Exp	Lit	Exp	Lit
Benzyl alcohol	298.15	1.0414	1.0412	38.63	38.58
2-Phenylethanol	298.15	1.062	—	39.43	—

Thermal expansion coefficient (α) and isothermal compressibility (β_T) values for the Flory model were obtained using an established equation. The mixing function ($\Delta\sigma$) can be represented mathematically by the Redlich-Kister polynomial [18] for correlating experimental data. The values of the coefficients were determined by multiple regression analysis based on the least squares method, and are summarized along with the standard deviations between the experimental and fitted values of the respective function (Table 2).

Table 2 Coefficients of the Redlich-Kister Equation and Standard Deviations (δ) for Surface Tension of Binary Liquid Mixtures at Various Temperatures

Benzyl alcohol+2-Phenyl ethanol					
T	A0	A1	A2	A3	Std dev(δ)
298.15K	-1.60	0.62	0.30	-0.54	0.016
308.15k	-1.40	0.35	0.50	-0.34	0.016
318.15k	-1.23	0.22	0.65	-0.24	0.017

McAllister coefficients a , b and c were calculated using the method of least squares, and standard deviations between the calculated and experimental values were determined (Table 3).

Table 3 Parameters of McAllister Three body and Four body Interaction Models and Standard Deviations (δ) for Surface Tension of Binary Liquid Mixtures at Various Temperatures

McAllister three Body Model/ (dyne/cm ²)				McAllister four Body Model/(dyne/cm ²)			
Benzyl alcohol+2-Phenyl ethanol							
T	a	b	(δ)/mN.m ⁻¹	a	b	c	(δ)/mN.m ⁻¹
298	16.90	23.84	0.05	38.93	38.21	39.11	0.10
308	16.55	23.52	0.07	38.14	37.54	38.63	0.09

318	16.18	23.12	0.08	37.25	36.82	37.98	0.07
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The data for the liquid mixtures (Tables 4-5) were evaluated. As the amount-of-substance fraction increases, the values of surface tension, molar volume and density decrease at all the three temperatures. Conversely, the values of excess volume also decrease as the amount-of-substance fraction increases up to a certain limit then increases continuously. The similar trend were observes for the binary system at all temperatures. The average deviation values in the surface tension were calculated for the different models (Table 4).

Table 4 Comparison of absolute average deviation values of surface tension obtained from various liquid state models

Benzyl alcohol+2-Phenylethanol

T/K	K _{as}	$\sigma_{ab}/$ mN. m ⁻¹	$\sigma_{Flory}/$ m N.m ⁻¹	$\sigma_{RA}/$ mN .m ⁻¹	$\sigma_{Glinsky}$ / m N .m ⁻¹	$\sigma_{McAllister}$ - body / m N.m ⁻¹	σ_{McA} - lister- body/ m N.m ⁻¹
298	0.20	38.9	9.90	2.38	3.92	0.09	0.20
308	0.10	38.9	7.84	1.03	2.35	0.15	0.19
318	0.06	37.9	5.75	0.49	1.58	0.18	0.14

RA model assuming association gave better results than Flory model assuming non-association. McAllister three and four body interaction models provide excellent results. In general, average results follow the order; McA-3 < McA-4 < RA < Glinsky < Flory.

Plot were constructed for the changes in surface tension with the amount-of-substance fraction at various temperatures using different models (Figures 1).

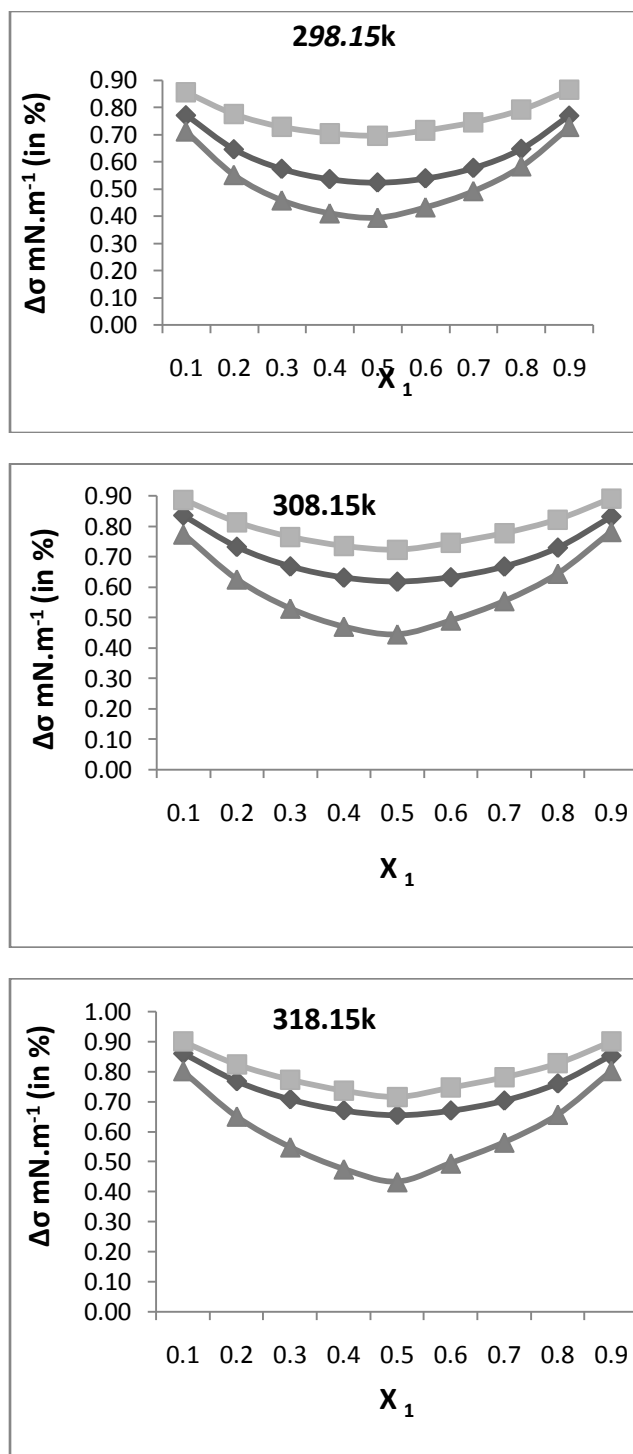


Figure 1 Changes in the surface tension ($\Delta\sigma$) with the amount-of-substance fraction (x_1) for benzyl alcohol+(1-x) 2-phenyl ethanol at 298.15, 308.15, and 318.15 K. Results were obtained using the following models: : black diamond, Flory model , black square, Ramaswamy and Anbananthan model , and black triangle, model suggested by Glinski .

In all the cases, the RA model showed lower changes in the surface tension than the Flory model. The model suggested by Glinski gave comparative better results than the Flory model. The trends observed in all the figures were similar and showed negative changes with increasing temperature, which indicates stronger interactions between the liquid molecules at higher temperatures. Figure shows that the surface tension deviations, $\Delta\sigma$, are positive. McAllister three and four body interactive models (McA-3, McA-4), show least deviations. The surface tension deviation values, $\Delta\sigma$, at about ($x = 0.3-0.5$) follow the order; Flory model > RA model > Glinski > McA-3 > McA-4. Positive deviations in surface tension for the system is a result of molecular association between hydroxyl and phenyl or benzyl groups resulting the formation of hydrogen bond and show the weak interactions between the components at all temperatures. For positive deviations association of molecules is more dominant than packing effect.

Excess volumes were evaluated by Flory model and the results were presented in Table 5. The values of excess volumes were plotted against the amount-of-substance fraction at three temperatures. Negative deviations of excess volumes with increasing temperature indicate stronger interactions between the liquid molecules at higher temperatures. Large positive deviations in excess volume values at all temperatures for the binary system are caused by strong interactions between alcoholic and phenyl or benzyl groups. It means the breaking of hydrogen bond and specific dipole-dipole interactions, as illustrated in the figures.

Conclusion:

Finally, it is concluded that computed results of surface tension from RA model assuming association gave better results than Flory model assuming non-association. McAllister three and four body interaction models provide excellent results for surface tension and excess volume and explained on the basis of packing effect, association properties and dipolar-dipolar interactions.

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Table 5 Molar Volume (V), Experimental Densities (ρ_{mix}), Experimental Surface Tensions (σ_{exp}), Theoretical Surface Tensions (σ_{theo}), Experimental Excess Volume (V_{exp}^E) and Theoretical Excess Volume (V_{Flory}^E) of Binary Liquid Mixtures at various temperatures

Benzyl alcohol+2-Phenylethanol

X_1	$V/\text{cm}^3\text{mol}^{-1}$	$\rho_{\text{mix}}/\text{g/cc}$	$\sigma_{\text{exp}}/\text{mN.m}^{-1}$	$\sigma_{\text{Flory}}/\text{mN.m}^{-1}$	$\sigma_{\text{RA}}/\text{mN.m}^{-1}$	$\sigma_{\text{Glinski}}/\text{mN.m}^{-1}$	$\sigma_{\text{McAllister-3}}/\text{mN.m}^{-1}$	$\sigma_{\text{McAllister-4}}/\text{mN.m}^{-1}$	$V_{\text{exp}}^E/\text{cm}^3\text{mol}^{-1}$	$V_{\text{theo}}^E/\text{cm}^3\text{mol}^{-1}$
298.15										
0.05	119.2985								-0.095	-0.09547
0.1	118.3739	1.0201	39.20	35.16	38.76	39.95	39.16	39.27	-0.201	-0.20145
0.15	117.4347								-0.322	-0.32214
0.2	116.5074	1.0245	39.00	35.10	38.22	40.35	38.95	39.08	-0.431	-0.43085
0.25	115.5851								-0.535	-0.5346
0.3	114.6832	1.0285	38.83	35.04	37.81	40.62	38.79	38.91	-0.618	-0.61785
0.35	113.8003								-0.682	-0.68221
0.4	112.9259	1.0321	38.70	34.98	37.53	40.74	38.67	38.78	-0.738	-0.73798
0.45	112.0633								-0.782	-0.78209
0.5	111.2292								-0.798	-0.7976
0.55	110.4368	1.0353	38.60	34.91	37.39	40.73	38.59	38.70	-0.771	-0.77136
0.6	109.6557								-0.734	-0.73396

0.65	108.9074	1.0373	38.60	34.85	37.37	40.57	38.55	38.66	-0.664	-0.66361
0.7	108.1685								-0.584	-0.58392
0.75	107.4481	1.0386	38.60	34.79	37.49	40.27	38.54	38.67	-0.486	-0.4858
0.8	106.7354								-0.38	-0.37988
0.85	106.0314	1.0394	38.60	34.72	37.74	39.84	38.55	38.69	-0.265	-0.26529
0.9	105.3288								-0.149	-0.14929
0.95	104.5955	1.0400	38.60	34.66	38.12	39.29	38.58	38.69	-0.064	-0.06409
308.15										
0.05	120.1577								-0.133	-0.13258
0.1	119.1953	1.0131	38.70	35.49	38.50	39.14	38.65	38.76	-0.27	-0.27041
0.15	118.2455								-0.396	-0.39578
0.2	117.3124	1.0174	38.48	35.39	38.14	39.27	38.41	38.56	-0.504	-0.50433
0.25	116.3832								-0.609	-0.60904
0.3	115.4781	1.0214	38.28	35.30	37.85	39.33	38.21	38.35	-0.69	-0.68958
0.35	114.5888								-0.755	-0.75441
0.4	113.7148	1.0250	38.10	35.21	37.62	39.32	38.05	38.17	-0.804	-0.8039
0.45	112.8481								-0.846	-0.84609
0.5	112.0071	1.0281	37.95	35.11	37.47	39.23	37.93	38.04	-0.863	-0.86261
0.55	111.2062								-0.839	-0.83896
0.6	110.4221	1.0301	37.90	35.01	37.38	39.07	37.84	37.96	-0.799	-0.79859
0.65	109.6596								-0.737	-0.73656
0.7	108.9088	1.0316	37.85	34.91	37.37	38.83	37.77	37.91	-0.663	-0.66283
0.75	108.1936								-0.554	-0.55353
0.8	107.4799	1.0322	37.80	34.82	37.42	38.53	37.74	37.88	-0.443	-0.44272
0.85	106.7791								-0.319	-0.31905
0.9	106.0785	1.0327	37.76	34.72	37.54	38.16	37.72	37.84	-0.195	-0.19509
0.95	105.3579								-0.091	-0.09125
318.15										
0.05	121.045								-0.165	-0.16477
0.1	120.040	1.0060	38.11	35.72	38.00	38.38	38.05	38.16	-0.339	-0.33904
0.15	119.077								-0.472	-0.4716
0.2	118.1322	1.0104	37.86	35.59	37.69	38.37	37.78	37.92	-0.586	-0.58585
0.25	117.2005								-0.687	-0.68685
0.3	116.2968	1.0143	37.63	35.47	37.43	38.32	37.55	37.68	-0.76	-0.76002
0.35	115.4076								-0.819	-0.81856
0.4	114.5305	1.0177	37.41	35.34	37.20	38.22	37.35	37.46	-0.865	-0.86506
0.45	113.6596								-0.905	-0.90535
0.5	112.8103	1.0207	37.21	35.20	37.02	38.08	37.18	37.29	-0.924	-0.92408
0.55	111.9996								-0.904	-0.90422
0.6	111.208	1.0228	37.12	35.07	36.88	37.89	37.04	37.16	-0.865	-0.86518
0.65	110.4374								-0.805	-0.80522
0.7	109.685	1.0243	37.02	34.94	36.79	37.66	36.93	37.06	-0.727	-0.72695
0.75	108.9613								-0.62	-0.6201
0.8	108.2528	1.0249	36.92	34.80	36.73	37.40	36.85	36.98	-0.498	-0.49795
0.85	107.5552								-0.365	-0.36499
0.9	106.8515	1.0252	36.84	34.67	36.72	37.09	36.79	36.89	-0.238	-0.2381
0.95	106.1418								-0.117	-0.11717