

## A Model for Correlation of Various Solvatochromic Parameters with Composition in Aqueous and Organic Binary Solvent Systems

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The applicability of the combined nearly ideal binary solvent/Redlich-Kister (CNIBS/R-K) equation for correlation of various solvatochromic parameters (SP) with composition is shown employing 84 experimental data sets for aqueous and organic binary solvent systems at temperatures ranging 15 to 75 °C. The model provides a simple computational model to correlate/predict different SP values in various binary solvent systems. In proposed equations, MPDs (mean percentage deviations) are between 0.0500% and 6.9591% in mixtures of dimethyl sulfoxide with 2-methylpropan-2-ol and benzene with 2-methylpropan-2-ol, respectively. Correlation of the calculated and experimental values of various SP give an equation with an overall mean percentage deviation (OMPD) of 1.1900,  $R^2 = 0.99692$ ,  $s.e = 0.01223$  and  $F = 341925.51$ . Approximately 70% of the calculated SP values have IPD (individual percentage deviation) lower than one and it is possible to predict unmeasured SP values by using only eight experimental data.

**Key Words :** Solvatochromic parameters, Redlich-Kister equation, Correlation equation

### Introduction

The energetic level of molecules may be modified by interactions with surrounding molecules and it may be difficult to relate chemical properties to molecular structures.<sup>1-5</sup> The solvent effects play a key role in many chemical and physical processes in solutions. The strong influence of solvent on chemical and physical processes (reaction rates, selectivity, chemical equilibria, position and intensity of spectral absorption bands and liquid chromatographic separations) has been well established.<sup>1</sup> The study of solute-solvent interactions in binary mixtures is more complex than in pure solvents, because the solute can interact to a different degree with the components of the mixture, and this difference in the interactions is reflected in the composition of the microsphere of solvation.<sup>6-15</sup>

The use of solvatochromic indicators is a suitable method for studying solute-solvent interactions, since the transition energy of the indicators depends on the solvation's sphere composition and properties.<sup>1,16</sup> The solvatochromic parameters ( $E_T(30)$ ,  $\pi^*$ ,  $\beta$  and  $\alpha$ ) are calculated from the maxima of absorbance of the indicators, expressed in wavenumber as  $kK$  ( $1 kK = 1000 \text{ cm}^{-1}$ ). The  $E_T(30)$  betaine dye is the solvatochromic indicator most widely used. It was proposed by Reichardt for measuring empirically the polarity of solvents. This indicator is sensitive to the dipolarity/polarizability ( $\pi^*$ ) and hydrogen-bond-donor capability ( $\alpha$ ) of the solvent. The Kamlet-Taft parameters of dipolarity/polarizability, hydrogen-bond donor acidity and hydrogen-bond acceptor basicity ( $\beta$ ) were calculated from the wavenumbers of maximum absorption of the UV-Vis spectroscopic shifts of appropriate solvatochromic indicators.<sup>17-20</sup>

The problem in studying solvent effects on various physico-

chemical properties is to identify and to assess the relative importance of various parameters of media on the properties of interest.<sup>8,11,13</sup> Solvatochromic parameters are demonstrated to be successful in correlating a wide range of chemical and physical properties involving solute-solvent interactions as well as biological activities of compounds.<sup>1,6-13</sup> Because of their empirical origins, their ability to make a priori predictions have been somewhat limited. Also infinite number of different solvent compositions can be prepared for particular binary solvent systems. For these reasons the prediction of solvatochromic parameters in mixed solvents based on a minimum number of experiments provides a useful computational tool.

In order to mathematically represent the effects of composition on the various solvatochromic parameters in mixed binary solvent systems, the combined nearly ideal binary solvent/Redlich-Kister (CNIBS/R-K) equation has been applied for experimental data of these parameters. This model has been used to correlate accurately different physico-chemical properties in mixed solvent systems: including solubility behavior of polycyclic aromatic hydrocarbons in binary organic solutions, solubility of drugs in water-cosolvent mixtures, multiple solubility maxima, solubility at various temperatures, chemical stability of drugs, acid dissociation constants of analytes, electrophoretic mobility of analytes and very recently dielectric constant of mixed solvents in binary and ternary solvent systems.<sup>21-33</sup> A theoretical basis for CNIBS/R-K model was provided earlier.<sup>21</sup>

The aim of this article is to evaluate the accuracy and applicability of the CNIBS/R-K model for calculating various solvatochromic parameters ( $E_T^N$ ,  $\alpha$ ,  $\pi^*$  and  $\beta$ ) in various aqueous and organic binary solvent systems, at temperatures ranging 15-75 °C.

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### Theoretical Treatment

The CNIBS/R-K model provides a simple method to correlate/predict the excess molar properties of a solute in a binary and ternary solvent systems in terms of weighted mole fraction average of solute properties in the pure solvents and contributions of solute-solvent and solvent-solvent interactions.<sup>21-33</sup>

The proposed model to calculate the solvatochromic parameters (SP) in a binary mixed solvent system at a constant temperature is expressed as:

$$SP_m = f_1 SP_1^0 + f_2 SP_2^0 + f_1 f_2 \sum_j M_j (f_2 - f_1)^j \quad (1)$$

in which  $SP_m$ ,  $SP_1^0$  and  $SP_2^0$  are solvatochromic parameters in mixed, pure solvents 1 and 2, respectively. Also  $f_1$  and  $f_2$  refer to volume fractions of binary solvent system.<sup>29</sup> One can use the mole/weight fractions of the solvents instead of the volume fractions. Although the numerical values of the curve-fitted parameters affected by employing mole/weight or volume fractions, in practice using the volume fractions in solvent blending is more common than the weight or mole fractions.  $M_j$  is model constant representing two-body and three-body interactional terms. The numerical values of  $j$  can be varied between 0-3 in order to present an accurate mathematical representation of experimental data. The numerical values of  $M_j$  can be computed by fitting the experimental values of  $SP_m - (f_1 SP_1^0 + f_2 SP_2^0)$  against  $f_1 f_2$ .

$f_1 f_2$ ,  $(f_2 - f_1)$ ,  $f_1 f_2 (f_2 - f_1)^2$  and  $f_1 f_2 (f_2 - f_1)^3$  by using no intercept multiparameter least squares analysis.<sup>32</sup> To assess the accuracy of the equations, the experimental values of the solvatochromic properties were fitted into the equation and the mean percentage deviation (MPD) between experimental and calculated values is considered as an accuracy criterion.

MPD defined as:

$$MPD = \frac{100}{N} \sum_{i=1}^N \left| \frac{SP_i^{exp} - SP_i^{cal}}{SP_i^{exp}} \right| \quad (2)$$

where  $N$  is the number of experimental data points in each set.  $SP_i^{exp}$  and  $SP_i^{cal}$  are experimental and calculated values of SP. The mean value of MPDs is denoted as overall MPD (OMPD) and is given by:

$$OMPD = \frac{1}{n} \sum_{i=1}^n MPD_i \quad (3)$$

where  $n$  is the number of experimental data sets.

The individual percentage deviation (IPD) is also calculated by:

$$IPD = 100 \times \left| \frac{SP_i^{exp} - SP_i^{cal}}{SP_i^{exp}} \right| \quad (4)$$

### Results and Discussion

In order to evaluate the accuracy of the proposed model,

**Table 1.** Results of correlations of various solvatochromic parameters (SP) with composition in aqueous and organic binary solvent systems at various temperatures<sup>a</sup>

No.	Binary solvent system	SP	N	t/°C	R <sup>2</sup>	F	s.e	MPD
1	Acetone + Water	E <sub>T</sub> <sup>N</sup>	18	25	0.99909	8623.12	0.021250	2.6780
2	Acetonitrile + Water	E <sub>T</sub> <sup>N</sup>	26	25	0.99866	18663.69	0.028570	3.0519
3	Dimethylformamide + Water	E <sub>T</sub> <sup>N</sup>	15	25	0.99983	82325.22	0.009591	1.1093
4	Dimethyl sulfoxide + Water	E <sub>T</sub> <sup>N</sup>	14	25	0.99954	27998.83	0.016010	1.8083
5	Ethylene glycol + Water	E <sub>T</sub> <sup>N</sup>	15	25	0.99993	189565.92	0.007709	0.6670
6	Ethanol + Water	E <sub>T</sub> <sup>N</sup>	21	25	0.99998	1046200.64	0.003579	0.3706
7	Ethanol + Water	α	21	25	0.99997	674567.26	0.005414	0.4011
8	Ethanol + Water	π*	21	25	0.99999	2168602.01	0.002931	0.2415
9	Ethanol + Water	β	21	25	0.99993	268196.66	0.006141	0.6807
10	Methanol + Water	E <sub>T</sub> <sup>N</sup>	21	25	0.99998	1040815.76	0.003861	0.3670
11	Methanol + Water	α	21	25	0.99998	868408.88	0.005350	0.3842
12	Methanol + Water	π*	21	25	0.99998	820058.09	0.004890	0.3990
13	Methanol + Water	β	21	25	0.99955	44394.40	0.013310	3.6412
14	2-Methylpropan-2-ol + Water	α	21	25	0.99943	35216.81	0.020850	1.9884
15	2-Methylpropan-2-ol + Water	π*	21	25	0.99980	99801.00	0.012660	1.0149
16	2-Methylpropan-2-ol + Water	β	21	25	0.99993	273729.35	0.006595	0.6443
17	Nitromethane + Water	E <sub>T</sub> <sup>N</sup>	8	25	0.99645	1963.12	0.045200	4.6559
18	Nitromethane + Water	E <sub>T</sub> <sup>N</sup>	8	50	0.99818	3846.69	0.031700	3.0597
19	Nitromethane + Water	E <sub>T</sub> <sup>N</sup>	8	75	0.99989	61149.43	0.007630	0.7703

<sup>a</sup>N is the number of data points in each set; F is fisher number; s.e is standard error of the estimate; and MPD is mean percentage deviation.

Table 1. Continued

No.	Binary solvent system	SP	N	t/°C	R <sup>2</sup>	F	s.e	MPD
20	Propan-1-ol + Water	E <sub>T</sub> <sup>N</sup>	21	25	0.99986	147093.53	0.009050	0.9232
21	Propan-2-ol + Water	E <sub>T</sub> <sup>N</sup>	21	25	0.99985	133033.33	0.009528	0.9280
22	Propan-2-ol + Water	α	21	25	0.99986	145529.92	0.010710	0.9376
23	Propan-2-ol + Water	π*	21	25	0.99940	33557.16	0.022760	2.0680
24	Propan-2-ol + Water	β	21	25	0.99989	179070.36	0.007885	0.8099
25	Acetonitrile + 2-Methylpropan-2-ol	E <sub>T</sub> <sup>N</sup>	7	25	0.99998	305351.60	0.0023300	0.3432
26	Acetonitrile + 2-Methylpropan-2-ol	E <sub>T</sub> <sup>N</sup>	7	50	1.00000	6440208.14	0.000480	0.0581
27	Acetonitrile + 2-Methylpropan-2-ol	E <sub>T</sub> <sup>N</sup>	7	75	0.99998	244908.00	0.002340	0.2814
28	Acetonitrile + Propan-1-ol	E <sub>T</sub> <sup>N</sup>	10	25	0.99986	66334.26	0.007590	0.8608
29	Acetonitrile + Propan-1-ol	E <sub>T</sub> <sup>N</sup>	10	50	0.99987	68440.15	0.007080	0.8903
30	Acetonitrile + Propan-2-ol	E <sub>T</sub> <sup>N</sup>	9	25	0.99995	159757.55	0.004260	0.5210
31	Acetonitrile + Propan-2-ol	E <sub>T</sub> <sup>N</sup>	9	50	0.99996	213705.71	0.003490	0.3917
32	Acetonitrile + Propan-2-ol	E <sub>T</sub> <sup>N</sup>	9	75	0.99992	98537.71	0.004820	0.6187
33	Benzene + Propan-2-ol	E <sub>T</sub> <sup>N</sup>	11	25	0.99974	38145.81	0.007489	1.3486
34	Benzene + Propan-2-ol	α	11	25	0.99829	5827.20	0.020480	3.4182
35	Benzene + Propan-2-ol	π*	11	25	0.99995	209162.71	0.004385	0.5162
36	Benzene + Propan-2-ol	β	11	25	0.99997	333003.74	0.003751	0.3904
37	Benzene + 2-Methylpropan-2-ol	E <sub>T</sub> <sup>N</sup>	18	30	0.99909	18749.20	0.010440	2.1598
38	Benzene + 2-Methylpropan-2-ol	α	18	30	0.99246	2238.02	0.023840	6.9591
39	Benzene + 2-Methylpropan-2-ol	π*	18	30	0.99995	313813.48	0.005606	0.8357
40	Dimethyl sulfoxide + Methanol	E <sub>T</sub> <sup>N</sup>	9	15	0.99999	787388.40	0.002200	0.2479
41	Dimethyl sulfoxide + Methanol	E <sub>T</sub> <sup>N</sup>	9	30	0.99999	2162199.42	0.001290	0.1660
42	Dimethyl sulfoxide + Methanol	E <sub>T</sub> <sup>N</sup>	9	50	0.99999	939163.01	0.001900	0.2145
43	Dimethyl sulfoxide + 2-Methylpropan-2-ol	E <sub>T</sub> <sup>N</sup>	8	25	1.00000	11881491.40	0.000373	0.0500
44	Dimethyl sulfoxide + 2-Methylpropan-2-ol	E <sub>T</sub> <sup>N</sup>	8	50	0.99999	1377049.69	0.001040	0.1690
45	Dimethyl sulfoxide + 2-Methylpropan-2-ol	E <sub>T</sub> <sup>N</sup>	8	75	0.99999	712722.50	0.001390	0.1970
46	Dimethyl sulfoxide + Propan-2-ol	E <sub>T</sub> <sup>N</sup>	10	25	0.99999	932392.42	0.001720	0.1893
47	Dimethyl sulfoxide + Propan-2-ol	E <sub>T</sub> <sup>N</sup>	10	50	1.00000	3077645.86	0.000897	0.1164
48	Dimethyl sulfoxide + Propan-2-ol	E <sub>T</sub> <sup>N</sup>	10	75	0.99999	1325769.02	0.001300	0.1922
49	Ethanol + Propan-2-ol	E <sub>T</sub> <sup>N</sup>	11	25	0.99999	1641387.65	0.001569	0.2030
50	Ethanol + Propan-2-ol	α	11	25	0.99987	75708.79	0.009447	0.8521
51	Ethanol + Propan-2-ol	β	11	25	0.99995	200032.11	0.006025	0.5567
52	Ethanol + 2-Methylpropan-2-ol	E <sub>T</sub> <sup>N</sup>	18	30	0.99999	2516423.14	0.001360	0.2102
53	Ethanol + 2-Methylpropan-2-ol	α	18	30	0.99991	196869.78	0.005690	0.8844
54	Ethanol + 2-Methylpropan-2-ol	β	18	30	0.99997	672548.08	0.004620	0.3900
55	Hexane + Propan-2-ol	E <sub>T</sub> <sup>N</sup>	10	25	0.99995	173387.04	0.003584	0.5553
56	Hexane + Propan-2-ol	α	10	25	0.99982	49372.93	0.009120	1.0346
57	Hexane + Propan-2-ol	π*	11	25	0.99991	115140.16	0.003363	1.3989
58	Hexane + Propan-2-ol	β	11	25	0.99966	29236.25	0.016200	1.2594
59	Hexane + 2-Methylpropan-2-ol	E <sub>T</sub> <sup>N</sup>	16	30	0.99994	260190.37	0.002780	0.6249
60	Hexane + 2-Methylpropan-2-ol	α	16	30	0.99940	25009.75	0.008430	1.6437
61	Hexane + 2-Methylpropan-2-ol	π*	18	30	0.99987	134197.52	0.004610	2.7635
62	Hexane + 2-Methylpropan-2-ol	β	18	30	0.99919	21093.43	0.023800	2.7561
63	Methanol + Acetonitrile	E <sub>T</sub> <sup>N</sup>	10	25	0.99955	20211.80	0.016030	1.4310
64	Methanol + Acetonitrile	E <sub>T</sub> <sup>N</sup>	10	50	0.99972	32212.14	0.012190	1.1020
65	Methanol + Propan-1-ol	E <sub>T</sub> <sup>N</sup>	10	25	0.99999	944844.38	0.002260	0.2496

**Table 1.** Continued

No.	Binary solvent system	SP	N	t/°C	R <sup>2</sup>	F	s.e	MPD
66	Methanol + Propan-1-ol	E <sub>T</sub> <sup>N</sup>	10	50	0.99996	204337.87	0.004676	0.4478
67	Methanol + Propan-2-ol	E <sub>T</sub> <sup>N</sup>	11	25	0.99994	164912.79	0.005531	0.5072
68	Methanol + Propan-2-ol	α	11	25	0.99979	46895.00	0.014200	0.9900
69	Methanol + Propan-2-ol	π*	11	25	0.99998	492494.55	0.002650	0.3083
70	Methanol + Propan-2-ol	β	11	25	0.99999	879727.87	0.002623	0.2679
71	Methanol + 2-Methylpropan-2-ol	E <sub>T</sub> <sup>N</sup>	18	30	0.99982	93336.38	0.007940	1.2695
72	Methanol + 2-Methylpropan-2-ol	α	18	30	0.99947	32100.86	0.017600	2.7427
73	Methanol + 2-Methylpropan-2-ol	β	18	30	0.99993	258258.84	0.006960	0.5987
74	2-Methylpropan-2-ol + propan-2-ol	E <sub>T</sub> <sup>N</sup>	18	30	1.00000	4394068.72	0.000914	0.1714
75	2-Methylpropan-2-ol + propan-2-ol	α	18	30	0.99994	274129.40	0.003769	0.6665
76	Nitromethane + Methanol	E <sub>T</sub> <sup>N</sup>	8	15	0.99959	16951.91	0.015900	1.6030
77	Nitromethane + Methanol	E <sub>T</sub> <sup>N</sup>	8	30	0.99960	17366.87	0.015300	1.5829
78	Nitromethane + Methanol	E <sub>T</sub> <sup>N</sup>	8	50	0.99968	22035.61	0.013100	1.3531
79	Nitromethane + 2-Methylpropan-2-ol	E <sub>T</sub> <sup>N</sup>	8	25	0.99999	879036.40	0.001470	0.1850
80	Nitromethane + 2-Methylpropan-2-ol	E <sub>T</sub> <sup>N</sup>	8	50	0.99999	1034411.42	0.001270	0.1640
81	Nitromethane + 2-Methylpropan-2-ol	E <sub>T</sub> <sup>N</sup>	8	75	0.99999	882814.60	0.001300	0.2147
82	Nitromethane + propan-2-ol	E <sub>T</sub> <sup>N</sup>	9	25	0.99993	113813.24	0.005080	0.6382
83	Nitromethane + propan-2-ol	E <sub>T</sub> <sup>N</sup>	9	50	0.99994	139287.81	0.004300	0.5468
84	Nitromethane + propan-2-ol	E <sub>T</sub> <sup>N</sup>	9	75	0.99998	456565.31	0.002220	0.3275

available various solvatochromic parameter data in various 24 aqueous and 60 organic binary solvent systems which published in recent years in temperatures ranging 15 to 75 °C were applied.<sup>34-40</sup> The details of the collected data including number of experimental data points in each sets (N), solvatochromic parameters (SP) and statistics of correlation equations along with MPD are shown in Table 1. To evaluate the correlation ability of the model, whole data points in each set have been fitted to the model and back-calculating SP values have been used to calculate MPDs. The experimental SP data for aqueous solutions of ethanol have been fitted to equation 1 and the trained equations obtained as:

$$E_T^N = 0.648f_1 + f_2 - 0.272(\pm 0.006) f_1f_2 - 0.135(\pm 0.024) f_1f_2(f_2 - f_1) + 0.340(\pm 0.029) f_1f_2(f_2 - f_1)^2 + 0.245(\pm 0.063) f_1f_2(f_2 - f_1)^3 \quad (5)$$

(n = 21, R<sup>2</sup> = 0.99998, s.e = 0.003579, F = 1046200.64, MPD = 0.3706)

$$\alpha = 0.980f_1 + 1.230f_2 - 0.964(\pm 0.01) f_1f_2 - 0.519(\pm 0.037) f_1f_2(f_2 - f_1) + 0.366(\pm 0.044) f_1f_2(f_2 - f_1)^2 + 1.229(\pm 0.095) f_1f_2(f_2 - f_1)^3 \quad (6)$$

(n = 21, R<sup>2</sup> = 0.99997, s.e = 0.005414, F = 674567.26, MPD = 0.4011)

$$\pi^* = 0.51f_1 + 1.14f_2 + 0.537(\pm 0.005) f_1f_2 + 0.317(\pm 0.02) f_1f_2(f_2 - f_1) + 0.380(\pm 0.024) f_1f_2(f_2 - f_1)^2 - 0.876(\pm 0.051) f_1f_2(f_2 - f_1)^3 \quad (7)$$

(n = 21, R<sup>2</sup> = 0.99999, s.e = 0.002931, F = 2168602.01, MPD = 0.2415)

$$\beta = 0.83f_1 + 0.49f_2 + 0.156(\pm 0.008) f_1f_2 - 0.181(\pm 0.02) f_1f_2(f_2 - f_1) \quad (8)$$

(n = 21, R<sup>2</sup> = 0.99993, s.e = 0.006141, F = 268196.66, MPD = 0.6807)

As can be seen from the statistics of the proposed equations, the model is statistically valuable. In Table 2, the experimental and calculated values of E<sub>T</sub><sup>N</sup>, α, π\* and β in aqueous solutions of ethanol along with IPD have been shown in various volume fraction of ethanol (f<sub>2</sub>) at 25 °C.

Correlative equations at various temperatures are also acceptable. For example these equations in solutions of methanol with dimethyl sulfoxide are as follow:

$$t = 15 \text{ }^\circ\text{C}$$

$$E_T^N = 0.449f_1 + 0.766f_2 + 0.427(\pm 0.008) f_1f_2 + 0.186(\pm 0.003) f_1f_2(f_2 - f_1) + 0.162(\pm 0.036) f_1f_2(f_2 - f_1)^2 + 0.171(\pm 0.076) f_1f_2(f_2 - f_1)^3 \quad (9)$$

(n = 9, R<sup>2</sup> = 0.999999, s.e = 0.002198, F = 787388.40, MPD = 0.2479)

$$t = 30 \text{ }^\circ\text{C}$$

$$E_T^N = 0.440f_1 + 0.749f_2 + 0.416(\pm 0.005) f_1f_2 + 0.157(\pm 0.018) f_1f_2(f_2 - f_1) + 0.08947(\pm 0.021) f_1f_2(f_2 - f_1)^2 + 0.09793(\pm 0.045) f_1f_2(f_2 - f_1)^3 \quad (10)$$

(n = 9, R<sup>2</sup> = 0.999996, s.e = 0.001292, F = 2162199.42, MPD = 0.1660)

$$t = 50 \text{ }^\circ\text{C}$$

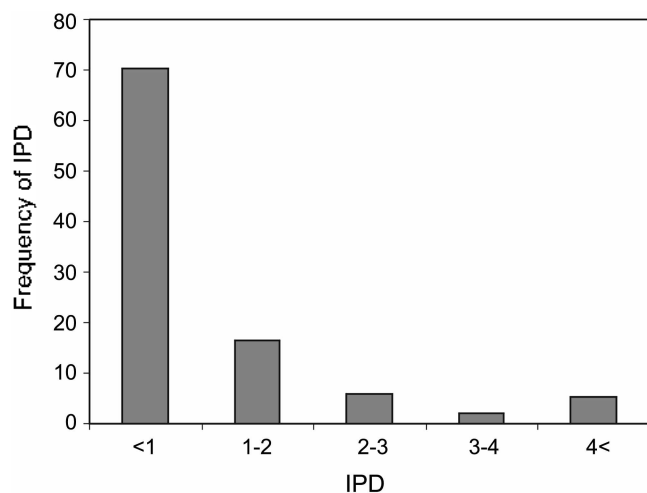
$$E_T^N = 0.427f_1 + 0.733f_2 + 0.369(\pm 0.006) f_1f_2 + 0.155(\pm 0.012) f_1f_2(f_2 - f_1) + 0.09212(\pm 0.027) f_1f_2(f_2 - f_1)^2 \quad (11)$$

(n = 9, R<sup>2</sup> = 0.999991, s.e = 0.001897, F = 939163.01, MPD = 0.2145)

**Table 2.** The experimental and calculated values of different solvatochromic parameters ( $E_T^N$ ,  $\alpha$ ,  $\pi^*$  and  $\beta$ ) in various volume fractions of aqueous solutions of ethanol ( $f_2$ ) along with IPD (individual percentage deviation) at 25 °C

$f_2$	$E_T^N$			$\alpha$			$\pi^*$			$\beta$		
	Exp.	Calc.	IPD	Exp.	Calc.	IPD	Exp.	Calc.	IPD	Exp.	Calc.	IPD
0.00	1.000	1.000	0.0000	1.230	1.230	0.0000	1.140	1.140	0.0000	0.490	0.490	0.0000
0.05	0.981	0.985	0.4357	1.200	1.206	0.5135	1.130	1.132	0.1634	0.500	0.507	1.3345
0.10	0.960	0.961	0.1535	1.160	1.159	0.1219	1.130	1.130	0.0287	0.530	0.525	0.9419
0.15	0.933	0.932	0.0614	1.100	1.100	0.0107	1.130	1.128	0.2044	0.540	0.545	0.8770
0.20	0.904	0.901	0.3129	1.040	1.039	0.0489	1.120	1.122	0.1755	0.560	0.566	0.9971
0.25	0.874	0.870	0.4550	0.990	0.984	0.6005	1.110	1.110	0.0169	0.590	0.587	0.4608
0.30	0.841	0.841	0.0408	0.940	0.938	0.2362	1.090	1.091	0.1278	0.610	0.610	0.0728
0.35	0.811	0.814	0.3912	0.900	0.903	0.3124	1.070	1.066	0.4016	0.630	0.632	0.3392
0.40	0.784	0.791	0.9151	0.870	0.880	1.1036	1.030	1.034	0.3944	0.660	0.655	0.7952
0.45	0.773	0.772	0.1500	0.870	0.867	0.3132	1.000	0.998	0.2023	0.670	0.677	1.0642
0.50	0.760	0.756	0.5263	0.860	0.864	0.4651	0.960	0.959	0.0781	0.700	0.699	0.1429
0.55	0.746	0.743	0.3751	0.870	0.867	0.3038	0.920	0.920	0.0305	0.720	0.720	0.0125
0.60	0.729	0.733	0.5204	0.880	0.875	0.6016	0.880	0.881	0.1129	0.750	0.740	1.3163
0.65	0.723	0.724	0.1370	0.890	0.884	0.7240	0.840	0.844	0.4992	0.770	0.759	1.4489
0.70	0.717	0.716	0.1463	0.890	0.892	0.2175	0.810	0.810	0.0391	0.770	0.776	0.7745
0.75	0.710	0.708	0.3026	0.900	0.899	0.1380	0.780	0.777	0.4087	0.790	0.791	0.1543
0.80	0.702	0.699	0.4335	0.890	0.904	1.5945	0.750	0.744	0.8466	0.790	0.804	1.8147
0.85	0.683	0.689	0.8339	0.910	0.910	0.0032	0.700	0.707	0.9608	0.810	0.815	0.6227
0.90	0.673	0.677	0.5549	0.930	0.920	1.0691	0.660	0.661	0.1152	0.830	0.823	0.8347
0.95	0.670	0.663	1.0375	0.940	0.940	0.0449	0.600	0.598	0.2650	0.830	0.828	0.2232
1.00	0.648	0.648	0.0000	0.980	0.980	0.0000	0.510	0.510	0.0000	0.830	0.830	0.0000

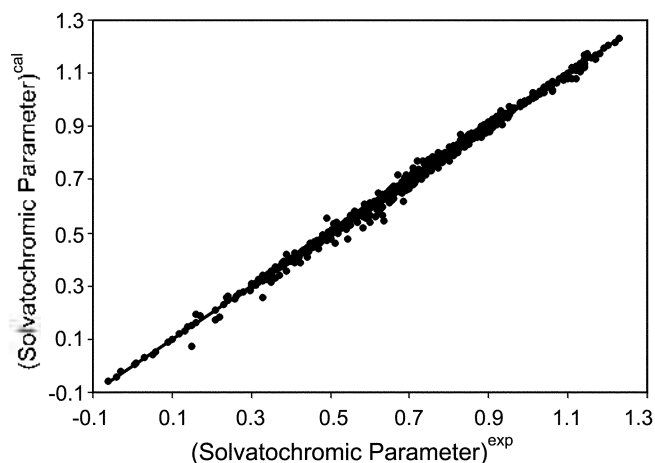
The distribution of IPD values for the correlative equations in different groups (IPD < 1, 1-2, 2-3, 3-4 and >4%) have been shown in Figure 1. As can be seen approximately 70% of the calculated SP values have IPD lower than 1%. For the correlation equations the least MPD value (0.0500%) has been observed for mixtures of dimethyl sulfoxide with 2-methylpropan-2-ol in correlation of  $E_T^N$  with composition and the highest MPD value (6.9591%) has been observed for mixtures of benzene with 2-methylpropan-2-ol in correlation

**Figure 1.** Plot of frequency of individual percentage deviations (IPD) vs. different groups of IPD (IPD<1, 1-2, 2-3, 3-4 and >4) for the proposed equations.

of  $\alpha$  with composition. As can be seen from statistics of the equations ( $R^2$ , F, s.e and MPD), the proposed equations are very excellent (Table 1). In Figure 2 the calculated values of SP ( $E_T^N$ ,  $\alpha$ ,  $\pi^*$  and  $\beta$ ) in various binary solvent systems from equation 1 plotted vs. the experimental values of them. As can be seen the correlation is reasonable. For this correlation the following equation can be obtained:

$$SP^{cal} - 1.003(-0.002)SP^{exp} - 0.0036(+0.001) \quad (12)$$

(n = 1060,  $R^2 = 0.99692$ , s.e = 0.01223, F = 341925.51, MPD = 1.1900)

**Figure 2.** Plot of the calculated values of SP from the correlation equations vs. the experimental values of it for various aqueous and organic binary solvent systems.

As expected, the model shows a strong correlation between predicted and experimentally measured values. The model did not show proportional and systematic error, because the slope ( $a = 1.003$ ) and intercept ( $b = 0.0036$ ) are not significantly different from unity and zero, respectively. It can be concluded that the CNIBS/R-K model is a good model to predict solvatochromic parameters of different aqueous and organic binary solvent systems in various compositions.

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