ELSEVIER

International Journal of Pharmaceutics 140 (1996) 237–246

international journal of pharmaceutics

Notes

Models for calculating solubility in binary solvent systems

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Received 21 February 1996; accepted 28 March 1996

Abstract

Two empirical models which express the relationship between the solute solubility and the concentration of one of the solvents in a binary solvent system are presented. The proposed models have been compared with previous similar models similar either in their original or modified forms from accuracy and predictability points of view using many experimental data taken from the literature. Both models were in some respects superior to the original and modified forms of the previous models. The modification of some of the previous models has improved the accuracy of the original models.

Keywords: Solubility; Binary solvent system; Cosolvency; Models for calculation

The use of solvent mixtures for affecting solubility has several applications in different fields of the pharmaceutical sciences including the formulation of liquid dosage forms. The quantification of drug solubility in the solvent mixtures enables one to predict and calculate the mixture composition for an optimum drug formulation. Several models are available for the calculation of the solubility in the solvent mixtures. In some models the solubility has been expressed in terms of the physicochemical properties of the solute and solvent system (Yalkowsky et al., 1975; Martin et al., 1980; Acree et al., 1991; Acree and Tucker, 1994; Barzegar-Jalali et al., 1996). In other models, the relation between the solubility and the concentration of the solvents in a binary solvent system has been provided (Yalkowsky and Roseman, 1981; Williams and Amidon, 1984; Ochsner et al., 1985, Acree et al., 1991; Barzegar-Jalali and Hanaee, 1994).

In the present work, two empirical equations which express the relationship between the solubility and the concentration of one of the solvents

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PII S0378-5173(96)04557-7

in a binary solvent system are given. The accuracy and predictability of the proposed equations are compared with those of the three-suffix excess free energy model (Williams and Amidon, 1984), mixture response-surface methodology (Ochsner et al., 1985) and nearly ideal binary solvent (NIBS)/Redlich–Kister model (Acree et al., 1991) as well as the modifications of the NIBS/Redlich–Kister model and the three-suffix excess free energy methods.

The proposed models are as follows:

$$\log(-logX_m) = A_{-3}10^{-3f_a} + A_{-1}10^{-f_a} + A_0 + A_1 10^{f_a} + A_3 10^{3f_a} \quad (1)$$

$$\log(-logX_m) = B_{-2}(\log f_a)^{-2} + B_{-1}(\log f_a)^{-1} + B_0 + B_1(\log f_a) + B_2(\log f_a)^2 \quad (2)$$

where X_m is the mole fraction solubility in the mixed solvent system, f_a denotes the concentration of one of the solvents in the binary solvent mixture expressed in volume and/or mole fraction, and the terms A and B are the parameters or constants of the models. Eq. (1) is applicable to all values of f_a from 0 to 1 whereas Eq. (2) holds for $0 < f_a < 1$.

The previously published equations which provide the relation between mole fraction solubility of the solute and concentrations of the solvents in the binary solvent system are the three-suffix excess free energy model (Eq. (3)), mixture response-surface methodology (Eq. (4)) and NIBS/Redlich–Kister model (Eq. (5)):

$$\log X_m = f_a logX_a + f_b logX_b + W_1 f_a f_b(2f_a - 1) + W_2 f_a^2 f_b + W_3 f_a f_b \quad (3)$$

$$\log X_m = \beta_1 f'_a + \beta_2 f'_b + \beta_3 / f'_a + \beta_4 / f'_b + \beta_5 f'_a f'_b \quad (4)$$

$$\log X_m = f_a logX_a + f_b logX_b + f_a f_b[S_0 + S_1(f_a - f_b) + S_2(f_a - f_b)^2] \quad (5)$$

where f_a and f_b represent the volume and/or mole fraction concentrations of the solvents a and b in the binary system, X_a and X_b are mole fraction solubilities of solute in the two neat solvents, W_1, W_2 and W_3 are constants of the model which equal $A_{1\text{-}3}\ q_2/q_1$, $2A_{3\text{-}1}\ q_2/q_3$ and C_2 in the original paper (Williams and Amidon, 1984), respectively. β_1–β_5 are coefficients of the model, f'_a and f'_b are given by: $f'_a = 0.96f_a + 0.02$ and $f'_b = 0.96f_b + 0.02$ (Ochsner et al., 1985), and S_0–S_2 are curve fitting parameters of the model.

In addition to the original models 3 and 5, the following modified forms of the models i.e. Eqs. (6) and (7) have been also used:

$$\log X_m = M_1 f_a + M_2 f_b + M_3 f_a f_b(2f_a - 1) + M_4 f_a^2 f_b + M_5 f_a f_b \quad (6)$$

$$\log X_m = J_1 f_a + J_2 f_b + f_a f_b[J_3 + J_4(f_a - f_b) + J_5(f_a - f_b)^2] \quad (7)$$

where M_1–M_5 and J_1–J_5 are model parameters.

Eqs. (1)–(7) were applied to solubility data for some solutes in the binary solvent systems taken from the literature. The details of the systems are given in Table 1.

In Table 2, the constants of Eq. (1) together with its coefficients of determination (R^2) and F-values are shown. For the sake of space, the model constants and statistical parameters of the other equations are not given.

The percent average error of the model predicted solubility with respect to the experimental solubility, %A.E., for each model was calculated by Eq. (8):

$$\%A.E. = 1/Z \sum |100[(X_m)_p - (X_m)_e]/(X_m)_e| \quad (8)$$

where Z equals the number of data, N, in each system for models 1 and 3–7 and $(N - 2)$ for the model 2, $(X_m)_p$ and $(X_m)_e$ denote the predicted and experimental values of X_m at f_a. The value of %A.E. was an indicator of the accuracy and predictability of the model. The lower the %A.E., the greater the accuracy of the model. The percent overall average error i.e. the sum of %A.E. divided by the total system number, %O.A.E. = (Σ%A.E.)/88, and the number of the systems adhered best to a model, judged from the number of the lower %A.E. values, were used for comparison of the models.

Table 1
Systems used for application of Eqs. (1)–(7)

System No.	Solute in solvent *a* + solvent *b*	Reference
1	Anthracene in benzene + cyclohexane	Acree and Rytting (1983)
2	Anthracene in benzene + n-heptane	Acree and Rytting (1983)
3	Anthracene in benzene + isooctane	Acree and Rytting (1983)
4	Anthracene in cyclooctane + benzene	Acree and Rytting (1983)
5	Anthracene in cyclooctane + cyclohexane	Acree and Rytting (1983)
6	Anthracene in dibutyl ether + n-hexadecane	McCargar and Acree (1987a)
7	Anthracene in dibutyl ether + squalane	McCargar and Acree (1987a)
8	Anthracene in n-heptane + cyclohexane	Acree and Rytting (1983)
9	Anthracene in n-hexane + benzene	Acree and Rytting (1983)
10	Anthracene in n-hexane + cyclohexane	Acree and Rytting (1983)
11	Anthracene in isooctane + cyclohexane	Acree and Rytting (1983)
12	Anthracene in n-octane + cyclohexane	Acree and Rytting (1983)
13	Benzil in carbon tetrachloride + isooctane	Acree and Rytting (1982b)
14	Benzil in cyclohexane + cyclooctane	Acree and Rytting (1982b)
15	Benzil in cyclohexane + n-heptane	Acree and Rytting (1982b)
16	Benzil in cyclohexane + isooctane	Acree and Rytting (1982b)
17	Benzil in cyclohexane + n-octane	Acree and Rytting (1982b)
18	Benzil in cyclooctane + carbon tetrachloride	Acree and Rytting (1982b)
19	Benzil in n-octane + carbon tetrachloride	Acree and Rytting (1982b)
20	Benzoic acid in cyclohexane + carbon tetrachloride	Acree and Bertrand (1981)
21	*p*-Benzoquinone in cyclohexane + isooctane	Acree and Rytting (1982a)
22	*p*-Benzoquinone in cyclooctane + cyclohexane	Acree and Rytting (1982a)
23	*p*-Benzoquinone in n-dodecane + n-heptane	Acree and Rytting (1982a)
24	*p*-Benzoquinone in n-heptane + carbon tetrachloride	Acree and Rytting (1982a)
25	*p*-Benzoquinone in n-heptane + cyclohexane	Acree and Rytting (1982a)
26	*p*-Benzoquinone in n-octane + carbon tetrachloride	Acree and Rytting (1982a)
27	Butyl-*p*-aminobenzoate in propylene glycol + water	Rubino and Obeng (1991)
28	Butyl-*p*-hydroxybenzoate in propylene glycol + water	Rubino and Obeng (1991)
29	Caffeine in dioxane + water	Adjei et al. (1980)
30	Carbazole in dibutyl ether + chlorocyclohexane	McCargar and Acree (1989)
31	Carbazole in dibutyl ether + 1-chlorohexane	Acree and McCargar (1987)
32	Carbazole in dibutyl ether + 1-chlorooctane	McCargar and Acree (1989)
33	Carbazole in dibutyl ether + 1-chlorotetradecane	McCargar and Acree (1989)
34	Carbazole in dibutyl ether + cyclohexane	McCargar and Acree (1987b)
35	Carbazole in dibutyl ether + cyclooctane	McCargar and Acree (1987b)
36	Carbazole in dibutyl ether + n-heptane	McCargar and Acree (1987b)
37	Carbazole in dibutyl ether + n-hexadecane	McCargar and Acree (1987a)
38	Carbazole in dibutyl ether + n-hexane	McCargar and Acree (1987b)
39	Carbazole in dibutyl ether + isooctane	McCargar and Acree (1987b)
40	Carbazole in dibutyl ether + methyl-cyclohexane	McCargar and Acree (1987b)
41	Carbazole in dibutyl ether + n-octane	McCargar and Acree (1987b)
42	Carbazole in dibutyl ether + squalane	McCargar and Acree (1987a)
43	Carbazole in tetrahydropyran + t-butylcyclohexane	Acree et al. (1991)
44	Carbazole in tetrahydropyran + cyclohexane	Acree et al. (1991)
45	Carbazole in tetrahydropyran + n-heptane	Acree et al. (1991)

Table 1 (continued)

System No.	Solute in solvent *a* + solvent *b*	Reference
46	Carbazole in tetrahydropyran + n-hexadecane	Acree et al. (1991)
47	Carbazole in tetrahydropyran + n-hexane	Acree et al. (1991)
48	Carbazole in tetrahydropyran + isooctane	Acree et al. (1991)
49	Ethyl-*p*-aminobenzoate in propylene glycol + water	Rubino and Obeng (1991)
50	Ethyl-*p*-hydroxybenzoate in propylene glycol + water	Rubino and Obeng (1991)
51	*p*-Hydroxybenzoic acid in dioxane + water	Wu and Martin (1983)
52	Iodine in n-heptane + benzene	Acree (1983)
53	Iodine in n-hexadecane + n-heptane	Acree and Bertrand (1977)
54	Iodine in n-hexadecane + isooctane	Acree and Bertrand (1977)
55	Iodine in n-hexane + benzene	Acree (1983)
56	Iodine in isooctane + benzene	Acree (1983)
57	Methyl-*p*-aminobenzoate in propylene glycol + water	Rubino and Obeng (1991)
58	Methyl-*p*-hydroxybenzoate in propylene glycol + water	Rubino and Obeng (1991)
59	Naphthalene in acetonitrile + water	Khossravi and Connors (1992)
60	Naphthalene in ethylene glycol + water	Khossravi and Connors (1992)
61	Naphthalene in methanol + water	Khossravi and Connors (1992)
62	Paracetamol in ethyl acetate + methanol	Subrahmanyam et al. (1992)
63	Paracetamol in methanol + water	Subrahmanyam et al. (1992)
64	Propyl-*p*-aminobenzoate in propylene glycol + water	Rubino and Obeng (1991)
65	Propyl-*p*-hydroxybenzoate in propylene glycol + water	Rubino and Obeng (1991)
66	Sulphadiazine in dimethylformamide + water	Martin et al. (1982a)
67	Sulphamethazine in ethanol + water	Bustamante et al. (1994)
68	Sulphamethazine in ethyl acetate + ethanol	Bustamante et al. (1994)
69	Sulphanilamide in dioxane + water	Reillo et al. (1993)
70	Sulphanilamide in ethanol + water	Bustamante et al. (1994)
71	Sulphanilamide in ethyl acetate + ethanol	Bustamante et al. (1994)
72	Sulphisomidine in dioxane + water	Martin et al. (1985)
73	Sulphamethoxypyridazine in ethanol + water, 20°C	Bustamante and Escalera (1995)
74	Sulphamethoxypyridazine in ethanol + water, 25°C	Bustamante and Escalera (1995)
75	Sulphamethoxypyridazine in ethanol + water, 30°C	Bustamante and Escalera (1995)
76	Sulphamethoxypyridazine in ethanol + water, 35°C	Bustamante and Escalera (1995)
77	Sulphamethoxypyridazine in ethanol + water, 40°C	Bustamante and Escalera (1995)
78	Testosterone in chloroform + cyclohexane	Martin et al. (1982b)
79	Theobromine in dioxane + water	Martin et al. (1981)
80	Theophylline in acetonitrile + water	Khossravi and Connors (1992)
81	Theophylline in dioxane + water	Martin et al. (1980)
82	Theophylline in ethylene glycol + water	Khossravi and Connors (1992)
83	Theophylline in methanol + water	Khossravi and Connors (1992)
84	Tolbutamide in hexane + ethanol	Martin and Miralles (1982)
85	*p*-Tolylacetic acid in cyclohexane + n-hexane	Judy and Acree (1985)
86	*p*-Tolylacetic acid in n-heptane + cyclohexane	Judy and Acree (1985)
87	*p*-Tolylacetic acid in isooctane + cyclohexane	Judy and Acree (1985)
88	*p*-Tolylacetic acid in n-octane + cyclohexane	Judy and Acree (1985)

Table 2
Constants of Eq. (1) and its statistical parameters

System No.	A_{-3}	A_{-1}	A_0	A_1	A_3	R^2	F-value
1	−0.02727	0.12750	0.35281	−0.00545	0.000017	0.99996	14 038
2	−0.02304	0.09099	0.38916	−0.00939	0.000024	0.99999	40 014
3	−0.03525	0.11698	0.40070	−0.01061	0.000022	0.99989	4639
4	0.01427	−0.04848	0.35295	0.00948	−0.000020	0.99954	1077
5	−0.00430	0.02313	0.42991	−0.00114	0.000002	0.99785	232
6	−0.00055	−0.00324	0.38776	−0.00018	0.000004	0.98196	81
7	0.00492	−0.02823	0.38977	0.00020	0.000000	0.99893	1171
8	−0.00044	0.00852	0.43817	0.00141	−0.000005	0.95980	11
9	0.02365	−0.08766	0.38095	0.01145	−0.000026	0.99998	20 068
10	0.00234	−0.00212	0.44550	0.00192	−0.000004	0.99962	1317
11	0.00214	−0.01541	0.45908	0.00185	−0.000004	0.99965	1437
12	0.00027	0.01039	0.43729	−0.00031	0.000001	0.99774	220
13	−0.02740	0.09820	0.30552	−0.02787	0.000002	0.99993	18 451
14	0.00564	−0.01660	0.27222	0.00296	−0.000005	0.99994	7707
15	−0.00934	0.03576	0.31517	−0.00292	0.000005	0.99995	9504
16	−0.01175	0.04114	0.32294	−0.00377	0.000006	0.99996	11 489
17	−0.00326	0.02006	0.31652	−0.00310	0.000007	0.99991	5583
18	0.03108	−0.21629	0.21433	0.00934	−0.000022	0.99947	1426
19	0.00818	−0.28486	0.30875	0.00643	−0.000014	0.99999	134 151
20	0.01447	−0.11720	0.20291	0.01657	−0.000119	0.99998	46 765
21	−0.00456	0.01093	0.33056	0.00096	−0.000002	0.99296	70
22	0.00093	0.00796	0.33240	−0.00174	0.000006	0.99798	247
23	−0.00154	0.01509	0.32645	−0.00197	0.000005	0.99997	15 721
24	0.01072	−0.14166	0.28773	0.00872	−0.000023	0.99999	76 449
25	0.00093	0.00329	0.33526	0.00011	0.000001	0.99635	136
26	0.01092	−0.14776	0.29634	0.00598	−0.000014	0.99999	52 011
27	0.00690	−0.02959	0.79614	−0.09379	0.000161	0.99943	2652
28	0.19648	−0.59949	1.27192	−0.21082	0.000780	0.99961	3805
29	−0.02747	0.31098	0.14787	−0.00959	0.000230	0.99633	745
30	0.03405	0.05038	0.31518	0.00474	−0.000006	0.99848	988
31	0.02835	0.05125	0.33187	0.00283	−0.000004	0.99504	301
32	0.00253	0.09342	0.31811	0.00386	−0.000004	0.99925	2007
33	−0.02794	0.14048	0.29869	0.00700	−0.000021	0.99821	837
34	0.06850	0.09821	0.41192	−0.00804	0.000021	0.99905	1569
35	0.06371	0.08493	0.40334	−0.00784	0.000028	0.99920	1867
36	0.01691	0.16150	0.40248	−0.00640	0.000007	0.99962	3931
37	0.01135	0.10260	0.42437	−0.00913	0.000019	0.99953	3217
38	0.05015	0.11453	0.43128	−0.01084	0.000028	0.99916	1779
39	0.02985	0.14935	0.41997	−0.00907	0.000018	0.99946	2788
40	0.06723	0.08574	0.42686	−0.01119	0.000038	0.99989	13 186
41	0.04468	0.09911	0.43666	−0.01194	0.000035	0.99983	8956
42	−0.00664	0.09361	0.42117	−0.00686	−0.000001	0.99944	3570
43	0.10489	0.12291	0.35724	−0.03046	0.000072	0.99965	4230
44	0.12685	0.15532	0.31803	−0.02866	0.000089	0.99979	7164
45	0.11788	0.10686	0.38483	−0.03731	0.000115	0.99965	4269

Table 2 (continued)

System No.	A_{-3}	A_{-1}	A_0	A_1	A_3	R^2	F-value
46	0.06899	0.09100	0.40053	−0.03240	0.000052	0.99972	6245
47	0.16157	0.17562	0.26797	−0.01971	0.000049	0.99968	3954
48	0.09721	0.13672	0.39051	−0.03452	0.000078	0.99967	4531
49	−0.08570	0.20154	0.53605	−0.05557	0.000097	0.99938	2427
50	−0.06427	0.12209	0.61881	−0.07744	0.000190	0.99898	1470
51	0.00389	0.36707	0.19923	−0.06286	0.000417	0.99690	643
52	0.04238	−0.18444	0.24870	0.01201	−0.000016	0.99992	14 780
53	−0.00783	0.06055	0.28523	−0.00362	0.000011	0.99948	964
54	−0.05730	0.14476	0.24341	0.00381	−0.000030	0.99889	450
55	0.01647	−0.12733	0.21099	0.01873	−0.000041	0.99988	4309
56	0.02195	−0.17338	0.25705	0.01302	−0.000022	0.99991	11 506
57	−0.07936	0.19590	0.50377	−0.04296	0.000082	0.99951	3056
58	−0.07921	0.14800	0.55376	−0.07915	0.000236	0.99919	1848
59	−0.08323	0.00000	1.62029	−0.72567	0.066760	0.99941	4548
60	−0.04524	0.25036	0.68219	−0.00970	0.000036	0.99996	73 554
61	−0.03604	0.12290	0.88675	−0.09822	0.002779	0.99989	16 118
62	−0.05683	0.16412	0.01867	0.01208	0.000183	0.99645	631
63	−0.21701	0.58037	0.11587	−0.00279	−0.000004	0.99651	142
64	−0.06668	0.14990	0.61807	−0.06716	0.000073	0.99954	3280
65	−0.01966	−0.00628	0.76327	−0.09936	0.000257	0.99952	3101
66	0.09381	−0.07009	0.79644	−0.07906	0.000087	0.99988	18 790
67	0.01400	0.30100	0.43694	−0.01016	0.000125	0.99716	527
68	−0.02854	0.19950	0.31602	0.00524	0.000069	0.99121	253
69	−0.01566	0.28710	0.35058	−0.11477	0.000777	0.99571	638
70	−0.11113	0.42545	0.18867	−0.00017	0.000098	0.99777	783
71	−0.09812	0.37647	0.02437	0.02361	0.000014	0.99153	146
72	0.01748	0.21208	0.42336	−0.04349	0.000392	0.99689	1280
73	0.09490	0.02077	0.29049	0.05908	−0.000233	0.99974	1926
74	0.10897	−0.01876	0.31141	0.05306	−0.000194	0.99918	611
75	0.13736	−0.03572	0.29268	0.05361	−0.000192	0.99922	638
76	0.07315	0.08426	0.20945	0.06282	−0.000222	0.99940	838
77	0.14041	0.00971	0.22008	0.06044	−0.000206	0.99885	436
78	−0.37982	1.36699	−0.46157	0.01230	0.000008	0.99782	1146
79	−0.03763	0.28488	0.39634	0.00799	0.000021	0.99943	2639
80	0.10788	−0.06813	0.83473	0.00066	0.000047	0.99798	1482
81	−0.01795	0.24135	0.29695	−0.02468	0.000335	0.99723	1442
82	−0.03114	0.13230	0.75905	0.01231	−0.000065	0.99756	1228
83	−0.03207	0.14017	0.75257	0.01248	−0.000039	0.99814	1075
84	−0.00057	0.06201	0.15068	0.03526	−0.000047	0.98784	81
85	−0.01778	0.06950	0.27360	−0.00149	0.000007	0.99958	1184
86	0.00543	−0.02363	0.28476	0.00482	−0.000013	0.99994	8284
87	0.00120	−0.01456	0.28086	0.00554	−0.000013	0.99900	499
88	0.01050	−0.03787	0.29869	0.00157	0.000004	0.99982	2792

Table 3
Percent average error of model predicted solubility with respect to the experimental solubility, %A.E., of each system and the percent overall average error, %O.A.E., for models 1–7

System No.	Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (6)	Eq. (7)	N
1	0.22	0.02	0.03	0.07	0.01	0.03	0.02	7
2	0.14	0.00	0.08	0.07	0.06	0.09	0.07	7
3	0.43	0.13	0.27	0.35	0.28	0.29	0.28	7
4	0.59	0.37	0.63	0.61	0.68	0.68	0.69	7
5	0.35	0.39	0.33	0.31	0.30	0.34	0.34	7
6	0.21	0.12	0.20	0.28	0.20	0.21	0.19	11
7	0.26	0.18	0.26	0.21	0.22	0.27	0.25	10
8	0.26	0.10	0.25	0.26	0.22	0.27	0.25	7
9	0.19	0.03	0.23	0.12	0.06	0.25	0.06	7
10	0.10	0.01	0.07	0.09	0.06	0.07	0.07	7
11	0.19	0.09	0.14	0.12	0.13	0.15	0.15	7
12	0.19	0.14	0.19	0.23	0.18	0.20	0.20	7
13	0.51	0.23	0.64	0.53	0.47	0.67	0.49	10
14	0.07	0.00	0.07	0.07	0.07	0.08	0.08	7
15	0.10	0.00	0.13	0.08	0.10	0.14	0.09	7
16	0.11	0.00	0.09	0.05	0.05	0.10	0.04	7
17	0.09	0.00	0.13	0.08	0.06	0.15	0.06	7
18	0.98	0.16	0.96	0.94	0.95	0.99	0.97	8
19	0.15	0.10	0.19	0.19	0.14	0.19	0.15	9
20	0.10	0.12	3.72	0.11	3.63	0.12	0.11	9
21	0.06	0.04	0.11	0.06	0.06	0.13	0.07	7
22	0.22	0.02	0.24	0.17	0.20	0.26	0.21	7
23	0.04	0.01	0.07	0.07	0.06	0.08	0.06	7
24	0.12	0.08	0.30	0.26	0.21	0.33	0.22	8
25	0.05	0.02	0.08	0.04	0.05	0.08	0.05	7
26	0.12	0.05	0.18	0.23	0.17	0.18	0.18	7
27	5.17	4.77	4.42	5.85	5.44	4.78	4.86	11
28	5.59	8.65	14.13	18.47	5.18	14.29	4.30	11
29	2.64	2.10	7.17	1.74	5.99	7.04	3.99	16
30	0.59	0.82	1.66	1.70	0.75	1.61	0.75	11
31	1.16	1.32	1.65	2.07	0.78	1.68	0.85	11
32	0.54	0.35	0.59	1.08	0.50	0.63	0.46	11
33	0.78	1.18	1.42	1.01	0.72	1.46	0.75	11
34	2.44	1.04	6.71	2.73	6.24	6.45	3.70	11
35	1.79	1.23	5.70	2.20	3.93	5.61	2.48	11
36	1.55	0.64	3.09	1.72	2.76	3.13	2.12	11
37	1.14	0.72	1.90	1.34	1.33	1.96	1.21	11
38	2.64	1.47	6.28	2.46	4.21	6.10	3.77	11
39	2.00	1.19	4.26	1.86	3.36	4.38	2.76	11
40	0.82	0.62	6.11	2.95	2.62	6.10	1.74	11
41	0.77	1.02	4.47	2.91	1.35	4.50	1.35	11
42	1.15	0.68	1.13	1.17	1.13	1.15	1.15	13
43	2.37	1.07	9.77	3.01	6.64	9.79	4.86	11
44	1.86	0.48	11.18	3.27	5.87	11.51	4.84	11
45	2.80	2.81	13.00	4.56	10.21	12.25	6.13	11

Table 3 (continued)

System No.	Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (6)	Eq. (7)	*N*
46	1.95	3.52	6.61	2.93	4.13	6.26	3.12	12
47	2.20	1.13	12.94	3.19	6.58	13.67	6.34	10
48	2.56	0.81	9.96	0.99	5.42	10.28	4.80	11
49	4.98	5.00	3.56	7.23	3.92	3.62	3.26	11
50	6.49	10.36	4.98	9.35	4.84	5.16	5.27	11
51	4.49	3.64	9.24	2.89	6.92	8.52	5.12	13
52	0.43	0.18	0.42	0.39	0.64	0.48	0.43	10
53	0.42	0.35	0.39	0.37	0.43	0.41	0.40	7
54	0.68	0.31	1.51	0.30	1.02	1.58	0.86	7
55	0.48	0.00	0.39	0.31	0.36	0.42	0.36	7
56	0.47	0.44	0.40	0.44	0.41	0.42	0.44	9
57	3.49	3.39	2.78	5.05	2.47	2.82	2.13	11
58	5.11	7.08	3.17	9.26	3.81	3.41	3.42	11
59	3.30	8.11	8.33	4.51	2.96	7.44	3.28	12
60	1.18	4.19	2.29	1.55	1.52	1.93	1.41	18
61	1.63	1.71	10.24	3.75	3.67	1.67	1.61	12
62	1.97	2.26	6.44	4.22	3.35	6.11	3.12	14
63	6.09	0.00	5.40	4.04	3.88	5.82	4.00	7
64	4.68	4.92	3.81	6.80	3.89	3.92	3.79	11
65	4.83	7.74	5.21	10.26	4.64	5.52	4.69	11
66	3.44	3.65	8.90	8.25	2.35	8.61	2.20	14
67	4.36	1.48	10.55	2.96	11.31	9.49	4.87	11
68	3.77	2.85	4.30	4.04	4.55	4.76	4.24	14
69	6.53	4.43	14.93	3.59	25.53	10.42	9.08	16
70	3.56	2.83	3.14	3.87	2.65	3.24	3.16	12
71	2.38	1.09	1.80	2.99	2.19	2.00	1.84	10
72	5.18	3.40	21.29	4.99	25.44	14.85	9.02	21
73	1.60	2.09	0.34	2.26	0.37	0.34	0.28	7
74	2.67	3.14	1.61	3.45	1.01	1.68	1.17	7
75	2.68	0.06	4.08	1.11	5.12	4.54	4.65	7
76	2.28	0.68	3.36	1.43	4.08	3.72	3.67	7
77	2.87	2.34	4.26	1.09	5.43	4.57	4.59	7
78	11.26	19.26	6.78	5.23	9.32	6.26	5.79	15
79	1.69	0.86	2.15	2.28	1.96	2.33	1.91	11
80	2.77	12.14	17.64	11.86	5.78	16.42	2.90	17
81	2.96	3.36	12.31	1.96	8.48	10.80	5.83	21
82	1.89	2.35	3.01	2.41	3.33	3.02	1.86	17
83	1.73	2.71	5.89	3.26	1.58	5.16	1.41	13
84	6.03	5.78	6.05	4.97	5.84	5.98	5.97	9
85	0.28	0.00	0.17	0.24	0.19	0.19	0.19	7
86	0.09	0.00	0.40	0.12	0.41	0.19	0.15	7
87	0.43	0.00	0.36	0.30	0.34	0.38	0.36	7
88	0.14	0.00	0.33	0.15	0.13	0.36	0.13	7
%O.A.E	1.95	1.98	3.93	2.47	3.07	3.63	2.17	

N, number of data in each system.

In Table 3, the values of %A.E. and %O.A.E. are provided. According to this table, the accuracy of the models with respect to %O.A.E. decreased in the following order:Eq. (1) > Eq. (2) > Eq. (7) > Eq. (4) > Eq. (5) > Eq. (6) > Eq. (3)

Eq. (1) was the most accurate model (%O.A.E. = 1.95) and Eq. (3) was the least accurate(%O.A.E. = 3.93). It can be seen from the above order that when the original Eqs. (3) and (5) were modified to Eqs. (6) and (7), the accuracy was improved. For example, modification of Eq. (5) to Eq. (7) decreased the %O.A.E. from 3.07 to 2.17.

In terms of the number of systems adhered best to a model which could be inferred from Table 3, Eq. (2) was the best followed by Eqs. (7), (5), (1), (4), (3) and (6), respectively.

The analyses given for 88 systems suggested that because of lower percent overall average error, models 1 and 2 were superior to the previous models. In addition, the highest number of systems adhered best to model 2 indicating its suitability.

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