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非电解质水溶液黏度的关联

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摘 要：许多化工过程的设计需要估算含水体系的黏度，但目前的黏度关联方法用于含水体系时误差较大。今以作者所在课题组近期提出的非水液体混合物黏度关联方程为基础，通过引入形状因子，得出了一个非电解质水溶液的黏度方程。该方程可用于二元非电解质水溶液黏度的关联，且能利用二元黏度得到的关联参数推算三元非电解质水溶液的黏度。该方程对 54 个二元非电解质水溶液体系黏度(总计 2876 个黏度数据点)关联的总平均相对偏差为 4.60%；对 7 个三元非电解质水溶液体系黏度(总计 352 个黏度数据点)推算的总平均相对偏差为 3.75%。结果表明，该方程具有较高的关联精度和推算精度。

关键词：黏度；非电解质水溶液；形状因子：关联
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Correlation of Viscosity of Aqueous Non-Electrolyte Solutions

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Abstract: The viscosity estimation for aqueous solution is required in the design of many chemical processes. However, the estimation results obtained by using the methods available in the literatures are usually not satisfactory. In this paper, the shape factor was introduced to the viscosity correlation equation for the non-aqueous liquid mixtures, which was developed recently by our group, and a new viscosity equation for aqueous non-electrolyte solutions was obtained. The new equation could be used not only for the correlation of viscosity of binary aqueous non-electrolyte solutions, but also for the viscosity estimation of ternary aqueous non-electrolyte solutions by using the equation parameters correlated from binary mixtures. 54 binary aqueous non-electrolyte solution systems with 2876 viscosity data points were correlated by using this new equation, and the total average absolute deviation of the correlation is 4.60%. Furthermore, 7 ternary aqueous non-electrolyte solution systems with 352 viscosity data points were also estimated by using the new equation with the total average absolute deviation of 3.75%. The results indicate that this new equation is adequate for correlating the viscosity of binary aqueous non-electrolyte solutions and for estimating the viscosity of ternary aqueous non-electrolyte solutions.

Key words: viscosity; aqueous non-electrolyte solutions; shape factor; correlation

1 前 言

非电解质水溶液体系(如水/2-丙醇、水/二甲基亚砜和水/1,2-丙二胺等)由于受到氢键、疏水和偶极等作用的影响[1~5]，其过量黏度较大且随着组成的变化具有较大的非对称性，因此对非电解质水溶液黏度关联的难度较大。文献中已提出多种可用于非电解质水溶液黏度关联的方法[6~11]，但大多适用的体系有限，

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对较复杂的非电解质水溶液体系(如水 / 胺类)黏度的关联误差较大。其中，相对较好较具有代表性的是Martins、Cardoso和Barcia[10,11]基于Eyring反应速率理论和UNIQUAC方程提出的黏度关联方程(式(1)，以下称Martins-Cardoso-Barcia方程)：

$$\ln(\eta V)=\sum_{i=1}^{N}x_i\ln(\eta_i V_i)+\sum_{i=1}^{N}x_i\ln\left(\frac{\phi_i}{x_i}\right)+5\sum_{i=1}^{N}q_i x_i\ln\left(\frac{\lambda_i}{\phi_i}\right)-\sum_{i=1}^{N}q_i x_i\ln\left(\sum_{j=1}^{N}\lambda_j\exp\left(-\frac{u_{ji}-u_{ii}}{RT}\right)\right) \tag{1}$$

最近Fang和He[12]基于Eyring反应速率理论和Flory-Huggins方程，假设液体混合物中分子为刚性小球，提出了一个单参数二元液体混合物的黏度方程(式(2))：

$$\ln(\eta_{\mathrm{mix}})=\theta_1\ln(\eta_1)+\theta_2\ln(\eta_2)+x_1\ln\left(\frac{\theta_1}{x_1}\right)+x_2\ln\left(\frac{\theta_2}{x_2}\right)+\left(x_1V_1^{2/3}+x_2V_2^{2/3}\right)\frac{\theta_1\theta_2\chi_{12}}{RT} \tag{2}$$

$$\theta_1=\frac{x_1V_1^{2/3}}{x_1V_1^{2/3}+x_2V_2^{2/3}} \tag{3a}$$

$$\theta_2=\frac{x_2V_2^{2/3}}{x_1V_1^{2/3}+x_2V_2^{2/3}} \tag{3b}$$

式(2)中，χ_{12}为方程参数，θ_1和θ_2分别为组分 1 和 2 的表面积分数。式(2)对非水液体混合物黏度的关联精度较高，且能适用于混合物中组分分子间体积差异较大的体系(如离子液体 / 有机溶剂体系)，但是不适用于非电解质水溶液黏度的关联。为此，本文将对式(2)进行修正，提出一个适用于非电解质水溶液的黏度方程。

2 非电解质水溶液黏度方程的建立

2.1 二元非电解质水溶液黏度方程

在非电解质水溶液中，由于受到氢键、疏水和偶极等多种作用，分子的形状成为影响混合物黏度的一个重要因素，刚性小球的假设将导致较大的误差，为此考虑将分子形状的影响引入到黏度方程中。现引入分子的形状因子f，并定义分子摩尔表面积正比为形状因子f(分子为刚性小球时，$f=1$)。引入形状因子后，式(2)、(3)中，$x_1{V_1}^{2/3}$、$x_1{V_1}^{2/3}$被相应修正为$f_1x_1{V_1}^{2/3}$、$f_2x_2{V_2}^{2/3}$，式(2)、(3)变为式(4)、(5)：

$$\ln(\eta_{mix})=\theta_1^*\ln(\eta_1)+\theta_2^*\ln(\eta_2)+x_1\ln\left(\frac{\theta_1^*}{x_1}\right)+x_2\ln\left(\frac{\theta_2^*}{x_2}\right)+\left(f_1x_1V_1^{2/3}+f_2x_2V_2^{2/3}\right)\frac{\theta_1^*\theta_2^*\chi_{12}}{RT} \tag{4}$$

$$\theta_1^*=\frac{f_1x_1V_1^{2/3}}{f_1x_1V_1^{2/3}+f_2x_2V_2^{2/3}} \tag{5a}$$

$$\theta_2^*=\frac{f_2x_2V_2^{2/3}}{f_1x_1V_1^{2/3}+f_2x_2V_2^{2/3}} \tag{5b}$$

对于二元非电解质水溶液，不妨令组分 1 为水，用下标W表示。同时将各组分的形状因子(f_i)与水的形状因子(f_{W})之比定义为对比形状因子(β_i)，即$\beta_i=f_i/f_{\mathrm{W}}$；当$i=$W时，$\beta_{\mathrm{W}}=1$。从而

$$\ln(\eta_{\mathrm{mix}})=\theta_{\mathrm{W}}^*\ln(\eta_{\mathrm{W}})+\theta_2^*\ln(\eta_2)+x_{\mathrm{W}}\ln\left(\frac{\theta_{\mathrm{W}}^*}{x_{\mathrm{W}}}\right)+x_2\ln\left(\frac{\theta_2^*}{x_2}\right)+\left(x_{\mathrm{W}}V_{\mathrm{W}}^{2/3}+\beta_2x_2V_2^{2/3}\right)\frac{\theta_{\mathrm{W}}^*\theta_2^*\psi_{\mathrm{W}2}}{RT} \tag{6}$$

$$\theta_{\mathrm{W}}^*=\frac{x_{\mathrm{W}}V_{\mathrm{W}}^{2/3}}{x_{\mathrm{W}}V_{\mathrm{W}}^{2/3}+\beta_2x_2V_2^{2/3}} \tag{7a}$$

$$\theta_2^*=\frac{\beta_2x_2V_2^{2/3}}{x_{\mathrm{W}}V_{\mathrm{W}}^{2/3}+\beta_2x_2V_2^{2/3}} \tag{7b}$$

式(6)即为二元非电解质水溶液黏度的关联方程，β_2和$\psi_{\mathrm{W}2}$为方程参数，其中$\psi_{\mathrm{W}2}=f_{\mathrm{W}}\chi_{\mathrm{W}2}$。

2.2 三元非电解质水溶液黏度方程

对于三元非电解质水溶液，也令组分 1 为水，参照三元Flory-Huggins方程[13]的形式将式(6)扩展为三元形式，得到式(8)。

$$\ln(\eta_{\mathrm{mix}})=\theta_{\mathrm{W}}^{*}\ln(\eta_{\mathrm{W}})+\theta_{2}^{*}\ln(\eta_{2})+\theta_{3}^{*}\ln(\eta_{3})+x_{\mathrm{W}}\ln\left(\frac{\theta_{\mathrm{W}}^{*}}{x_{\mathrm{W}}}\right)+x_{2}\ln\left(\frac{\theta_{2}^{*}}{x_{2}}\right)+x_{3}\ln\left(\frac{\theta_{3}^{*}}{x_{3}}\right)+\left(x_{\mathrm{W}}V_{\mathrm{W}}^{2/3}+\beta_{2}x_{2}V_{2}^{2/3}+\beta_{3}x_{3}V_{3}^{2/3}\right)\frac{\left(\theta_{\mathrm{W}}^{*}\theta_{2}^{*}\psi_{\mathrm{W}2}+\theta_{\mathrm{W}}^{*}\theta_{3}^{*}\psi_{\mathrm{W}3}+\theta_{2}^{*}\theta_{3}^{*}\psi_{23}\right)}{RT} \tag{8}$$

$$\theta_{\mathrm{W}}^{*}=\frac{x_{\mathrm{W}}V_{\mathrm{W}}^{2/3}}{x_{\mathrm{W}}V_{\mathrm{W}}^{2/3}+\beta_{2}x_{2}V_{2}^{2/3}+\beta_{3}x_{3}V_{3}^{2/3}} \tag{9a}$$

$$\theta_{2}^{*}=\frac{\beta_{2}x_{2}V_{2}^{2/3}}{x_{\mathrm{W}}V_{\mathrm{W}}^{2/3}+\beta_{2}x_{2}V_{2}^{2/3}+\beta_{3}x_{3}V_{3}^{2/3}} \tag{9b}$$

$$\theta_{3}^{*}=\frac{\beta_{3}x_{3}V_{3}^{2/3}}{x_{\mathrm{W}}V_{\mathrm{W}}^{2/3}+\beta_{2}x_{2}V_{2}^{2/3}+\beta_{3}x_{3}V_{3}^{2/3}} \tag{9c}$$

式(8)即为三元非电解质水溶液的黏度方程，β_2、β_3、$\psi_{\mathrm{W}2}$、$\psi_{\mathrm{W}3}$和ψ_{23}为方程参数。

对于二元非电解质水溶液体系，式(8)还原为式(6)；对于非水组分(2) / 非水组分(3)体系，式(8)可以简化为式(10)。

$$\ln(\eta_{\mathrm{mix}})=\theta_{2}^{*}\ln(\eta_{2})+\theta_{3}^{*}\ln(\eta_{3})+x_{2}\ln\left(\frac{\theta_{2}^{*}}{x_{2}}\right)+x_{3}\ln\left(\frac{\theta_{3}^{*}}{x_{3}}\right)+\left(\beta_{2}x_{2}V_{3}^{2/3}+\beta_{3}x_{3}V_{3}^{2/3}\right)\frac{\theta_{2}^{*}\theta_{3}^{*}\psi_{23}}{RT} \tag{10}$$

$$\theta_{2}^{*}=\frac{\beta_{2}x_{2}V_{2}^{2/3}}{\beta_{2}x_{2}V_{2}^{2/3}+\beta_{3}x_{3}V_{3}^{2/3}} \tag{11a}$$

$$\theta_{3}^{*}=\frac{\beta_{3}x_{3}V_{3}^{2/3}}{\beta_{2}x_{2}V_{2}^{2/3}+\beta_{3}x_{3}V_{3}^{2/3}} \tag{11b}$$

形状因子只有在关联和推算非电解质水溶液黏度时才被引入到黏度方程中，因此，式(10)不是一个独立的二元非水液体混合物黏度方程，而是一个在推算三元非电解质水溶液黏度时才使用的辅助方程，β_2、β_3和ψ_{23}为方程参数。

式(8)中的方程参数(β_2、β_3、$\psi_{\mathrm{W}2}$、$\psi_{\mathrm{W}3}$和ψ_{23})可通过关联相关的二元体系的黏度得到：利用式(6)关联水(1) / 非水组分(2)体系得到参数β_2、$\psi_{\mathrm{W}2}$；利用式(6)关联水(1) / 非水组分(3)体系的黏度得到参数β_3、$\psi_{\mathrm{W}3}$；将已得到的参数β_2和β_3代入式(10)，由式(10)关联非水分子(2) / 非水组分(3)体系的黏度得到参数ψ_{23}。从而，将上述参数代入式(8)就可以推算三元非电解质水溶液体系的黏度。

3　结果和讨论

3.1　二元水溶液黏度的关联

利用式(6)对 54 个二元非电解质水溶液体系的黏度(总计 2876 个黏度数据点)进行了关联，涉及的体系有水 / 醇、水 / 醇醚、水 / 胺、水 / 醇胺、水 / 酰胺、水 / 羧酸、水 / 腈、水 / 吡咯烷酮、水 / 亚砜、水 / 哌啶和水 / 吡咯烷。关联方程参数时，使平均相对偏差最小化。

表 1 给出了式(6)对二元非电解质水溶液黏度的关联结果，作为比较，同时给出了 Martins-Cardoso-Barcia 方程的关联结果。

由表 1 可见，式(6)的关联结果普遍好于 Martins-Cardoso-Barcia 方程，式(6)和 Martins-Cardoso-Barcia 方程的总平均相对偏差分别为 4.60%和 11.95%。作为示例，图 1 给出了本文式(6)和 Martins-Cardoso-Barcia 方程关联水 / 乙醇体系黏度的结果，可见，式(6)的关联结果与实验数据吻合很好，Martins-Cardoso-Barcia 方程的关联结果与实验数据偏差较大。从表 1 中还可以看出，水 / 含氮类体系特别是水 / 胺类体系的关联误差较大。式(6)和 Martins-Cardoso-Barcia 方程关联结果的平均绝对偏差(*AAD*)的最大值均出现在水 / 1,2-乙二胺体系，分别为 13.00%和 28.58%。图 2 给出了本文式(6)和 Martins-Cardoso-Barcia 方程关联水 / 1,2-乙二胺体系黏度的结果，可以看出式(6)的关联结果基本符合实验数据的趋势，而 Martins-Cardoso-Barcia 方程的关联精度较差。

表 1 本文式(6)和 Martins-Cardoso-Barcia 方程对二元非电解质水溶液黏度的关联结果

Table 1 Correlation results of this work eq. (6) and Martins-Cardoso-Barcia equation for viscosity of binary aqueous non-electrolyte solutions

Component (2) [a]	N_D	T / K	This work eq. (6)				Martins-Cardoso-Barcia eq.(1)				Ref.
			β_2	ψ_{W2}	AAD / % [b]	MaxAD / % [c]	$\frac{u_{21}-u_{11}}{R}$	$\frac{u_{12}-u_{22}}{R}$	AAD / %	MaxAD / %	
Methanol	60	283-323	1.84	871.0	4.54	15.23	1278.6	–4.0	5.55	19.79	[14]
Ethanol	70	283-323	3.01	828.2	6.57	25.98	4185.4	18.2	10.21	38.90	[14]
1-Propanol	45	303-323	3.27	614.6	1.76	6.37	6105.3	–89.2	7.63	21.52	[14]
2-Propanol	45	303-323	3.86	693.2	2.97	7.92	6109.8	–65.5	11.06	29.06	[2]
Ethylene glycol	44	283-313	1.39	56.1	1.59	6.55	563.0	41.5	2.69	6.39	[15]
1,2-Propanediol	126	298-338	1.67	–11.9	5.15	13.19	749.8	84.3	8.35	27.29	[16]
1,3-Propanediol	110	298-338	1.21	143.2	2.67	10.03	540.2	207.5	5.47	15.01	[16]
1,2-Butanediol	110	298-338	2.09	–14.9	6.65	21.05	992.1	136.1	13.47	38.01	[16]
1,4-Butanediol	110	298-338	3.18	37.7	7.77	21.74	4440.5	414.8	19.06	46.16	[16]
2,3-Butanediol	110	298-338	1.49	–149.0	7.08	18.87	204.2	154.0	11.66	31.38	[16]
Diethylene glycol	9	298	1.21	428.8	0.28	0.62	2657.8	422.6	3.80	6.60	[17]
EGMME	9	298	2.50	816.9	1.80	3.01	4822.0	72.7	7.98	14.57	[17]
EGMEE	9	298	2.85	885.1	0.95	1.52	3525.4	144.7	10.66	22.87	[17]
EGMBE	36	283-313	2.82	804.9	2.06	6.24	4465.0	190.7	10.69	36.29	[18]
DEGMEE	60	283-333	2.33	811.0	5.43	18.19	4791.2	275.3	13.42	41.47	[19]
DEGMBE	45	283-323	2.64	820.2	3.09	10.11	3304.8	344.8	14.07	47.74	[18]
TEGMEE	70	293-333	2.47	801.6	4.91	19.00	3155.2	402.4	17.36	50.69	[20]
TEGMBE	75	293-333	2.64	811.1	2.49	8.61	3133.4	446.6	19.22	50.12	[21]
DEGDEE	26	293	4.21	1093.3	9.75	18.06	5143.6	162.2	26.57	42.55	[22]
E181	16	303	4.64	949.9	3.22	6.96	4784.7	242.3	21.23	46.82	[23]
Ddipropylene glycol	5	313	1.36	418.3	0.51	1.24	4330.4	644.9	5.40	17.69	[24]
Tripropylene glycol	5	313	1.51	699.2	0.33	0.83	6182.9	981.1	11.36	35.54	[24]
PGME	44	298-328	2.52	889.4	4.61	13.35	6080.2	120.3	10.07	32.04	[25]
Tetrahydrofuran	50	303-323	4.75	985.7	4.36	11.85	6013.9	–244.5	12.23	25.48	[3]
1,4-Dioxane	36	293-313	2.57	679.3	4.01	8.56	6098.5	–187.3	7.81	17.50	[4]
Acetone	71	293-323	4.55	1047.1	5.21	14.68	6003.7	–243.8	10.62	24.07	[14]
DAA	9	323	1.90	808.2	1.34	2.83	3012.0	167.8	4.32	8.72	[26]
Acetic acid	33	293-303	0.62	1096.6	3.26	6.69	253.2	446.7	2.34	5.57	[27]
Isobutyric	110	302-313	2.00	950.6	3.11	9.64	3632.6	184.3	6.29	17.50	[28]
Acetonitrile	13	298	5.01	767.7	2.48	6.55	–256.5	256.4	7.86	11.78	[29]
Ttriethylamine	54	283-291	3.83	1622.0	7.52	23.40	4475.7	314.6	27.09	52.79	[30]
Ethane-1,2-diamine	60	303-323	1.87	1489.7	13.00	29.54	5025.7	729.8	28.58	54.29	[31]
1,2-Diaminopropane	55	303-323	2.14	1449.3	12.05	28.29	5039.5	599.4	27.84	55.04	[31]
1,3-Diaminopropane	65	303-323	1.82	1390.1	11.90	28.95	5043.6	627.7	25.23	52.40	[31]
Monoethanolamine	32	303-318	0.92	827.6	3.06	7.52	799.4	479.9	5.69	14.44	[32]
MAE	66	298-343	1.24	1072.3	8.39	24.65	3255.3	696.6	15.34	46.62	[33]
DMEA	40	313-353	1.82	1138.1	8.34	25.20	6945.6	467.5	16.32	43.97	[34]
Diethanolamine	55	303-323	0.86	593.8	2.30	6.75	7346.4	1252.9	12.15	33.53	[35]
MDEA	60	303-323	1.13	857.0	4.22	12.66	4797.0	1524.1	21.76	49.01	[36]
Diisopropanolamine	48	318-343	1.04	583.0	1.86	6.81	6067.8	1430.3	16.30	42.71	[37]
AMP	44	313-343	1.05	630.4	2.79	9.61	1565.0	675.8	8.74	24.57	[38]
Trethanolamine	65	298-353	1.00	426.9	2.32	9.37	2907.3	1098.6	16.35	49.00	[39]
Diglycolamine	55	298-343	1.41	635.9	3.65	12.45	3413.6	510.2	11.55	38.96	[40]
N-Methylformamide	45	298-318	1.91	447.3	1.69	4.44	974.0	–147.4	2.53	6.85	[41]
DMF	84	293-353	1.99	829.2	8.16	30.70	990.7	–41.3	8.65	31.68	[42]
N-Methylacetamine	60	308-318	1.77	590.7	2.34	6.97	3353.3	107.2	4.49	14.00	[43]
DMA	9	298	2.95	1224.6	6.42	10.55	4155.5	225.1	17.50	29.31	[16]
2-Pyrrolidinone	95	298-338	1.50	388.3	3.65	9.79	856.0	106.0	6.94	21.82	[44]
NMP	95	298-338	1.92	936.3	11.83	32.39	2097.8	122.8	14.23	39.73	[44]
Allyl alcohol	45	303-323	3.47	604.3	1.05	4.66	3451.9	–189.3	5.11	14.90	[2]
Propargyl alcohol	45	303-323	2.45	323.8	0.46	1.47	1562.1	–309.4	1.59	5.38	[2]
Dimethyl sulfoxide	50	303-323	1.73	796.3	4.66	11.00	3360.0	89.2	6.79	16.25	[45]
Piperidine	48	293-323	1.61	1268.6	8.46	26.48	4758.7	373.0	12.49	39.99	[46]
Pyrrolidine	40	293-323	2.11	1263.9	8.51	20.97	4792.3	195.6	13.55	36.08	[46]
Total AAD / % [d]					4.60				11.95		

[a] EGMME, ethylene glycol monomethyl ether; EGMEE, ethylene glycol monoethyl ether; EGMBE, ethylene glycol monobutyl ether; DEGMEE, diethylene glycol monoethyl ether; DEGMBE, diethylene glycol monobutyl ether; TEGMEE, triethylene glycol monoethyl ether; DEGDEE, diethylene glycol diethyl ether; E181, tetraethylene glycol dimethyl ether; PGME, Propylene glycol monomethyl ether; DAA, 4-hydroxy-4-methyl-2-pentane; MAE, 2-(Methylamino) ethanol; DMEA, dimethylethanolamine; AMP, 2-amino-2-methyl-1-propanol; DMF, N,N-dimethylformamine; DMA, N,N-dimethylacetamine; NMP, 1-methyl-2-pyrrolidinone.

[b] AAD: average absolute deviation,. $$AAD/\% = \frac{1}{N_D}\sum_{i=1}^{N_D}\left(100\times\frac{\left|\eta_i^{cal}-\eta_i^{exp}\right|}{\eta_i^{exp}}\right)$$

[c] MaxAD: maximum absolute deviation, $$\mathrm{Max}AD/\% = \mathrm{Max}\left(100\times\frac{\left|\eta_i^{cal}-\eta_i^{exp}\right|}{\eta_i^{exp}}\right),\left(i=1,2\cdots N_D\right).$$

[d] total AAD: total average absolute deviation,. $$\text{total } AAD/\% = \frac{1}{N_{Syst}}\sum_{i=1}^{N_{Syst}} AAD_i/\%$$

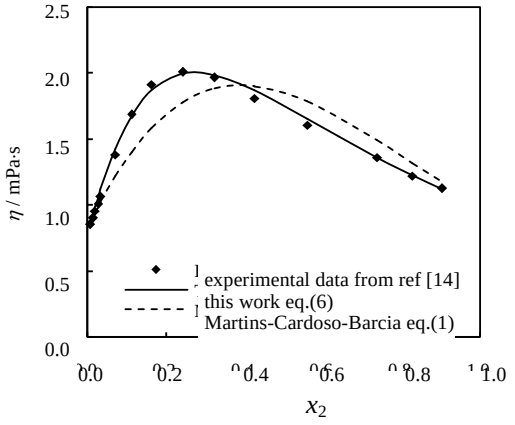

图 1　在 303 K 下对水(1) / 乙醇(2)体系黏度的关联结果

Fig.1　Correlation results of viscosity of water (1) / ethanol (2) at 303 K

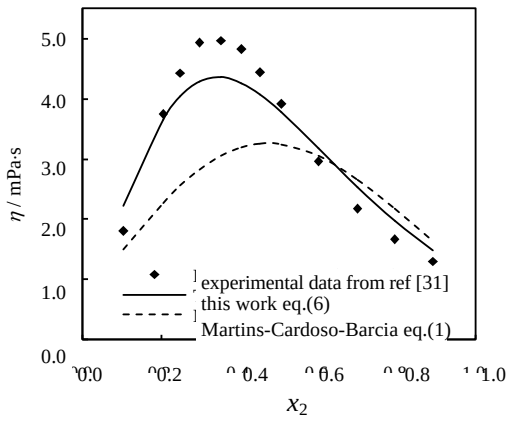

图 2　在 313 K 下对水(1) / 1, 2-乙二胺(2)体系黏度的关联结果

Fig.2　Correlation results of viscosity of water (1) / 1,2-diamino -ethane (2) at 313 K

3.2　三元水溶液黏度的推算

对于水(1) / 非水组分(2) / 非水组分(3)组成的三元非电解质水溶液，利用式(8)并结合二元黏度数据关联得到的参数就可推算三元非电解质水溶液的黏度。式(8)中参数β_2和ψ_{W2}、β_3和ψ_{W3}可以从表 1 中查到。将参数β_2和β_3用于式(10)，再用式(10)去关联非水组分(2) / 非水组分(3)体系的黏度可得到参数ψ_{23}。表 2 给出了式(10)和Martins-Cardoso-Barcia方程对非水组分(2) / 非水组分(3)体系黏度的关联结果。

表 2　本文式(10)和 Martins-Cardoso-Barcia 方程对二元非水液体混合物黏度的关联结果

Table 2　Correlation results of this work eq. (10) and Martins-Cardoso-Barcia equation for viscosity of binary non-aqueous liquid mixtures

Systems	N_D	T / K	This work eq. (10)		Martins-Cardoso-Barcia eq. (1)			Ref.
			ψ_{23}	*AAD* / %	$\frac{u_{32}-u_{22}}{R}$	$\frac{u_{23}-u_{33}}{R}$	*AAD* / %	
Mmethanol(2) /Ethanol(3)	94	283-323	−14.13	1.44	218.27	−143.27	0.67	[14]
Methanol(2) / 1-Propanol(3)	12	303.15	−38.14	2.43	304.26	−158.80	1.87	[14]
Ethanol(2) / 1-Propanol(3)	10	303.15	−4.71	0.38	42.23	−31.42	0.29	[14]
Methanol(2) / Acetone(3)	13	298.15	65.61	2.06	−203.72	202.17	1.79	[48]
2-Propanol(2) / DAA (3)	9	323.15	3.61	0.85	269.82	−187.48	0.17	[49]
1,4- Dioxane (2) / DMSO(3)	24	303-313	7.64	0.68	47.41	−90.06	1.93	[4]
DMF(2) / NMF(3)	11	298.15	−4.06	0.74	129.25	−129.55	0.75	[50]
Total *AAD* / %				1.23			1.06	

将关联二元黏度得到的参数β_2、β_3、ψ_{W2}、ψ_{W3}、ψ_{23}代入式(8)就可以推算得到三元非电解质水溶液体系的黏度。表 3 给出了式(8)对 7 个三元非电解质水溶液体系黏度(352 个黏度数据点)的推算结果，作为比较，表 3 同时给出了Martins-Cardoso-Barcia方程的推算结果。从表 3 可以看出，式(8)推算的平均绝对偏差的最大值出现在水(1) / 甲醇(2) / 乙醇(3)体系，为 6.61%；Martins-Cardoso-Barcia方程推算的平均绝对偏差的最大值出现在水(1) / 1,4-二噁烷(2) / 二甲基亚砜(3)体系，为 15.37%。式(8)和Martins-Cardoso-Barcia方程对三元非电解质水溶液推算的总平均相对偏差分别为 3.75%和 14.93%，式(8)对三元非电解质水溶液黏度推算的精度高于Martins-Cardoso-Barcia方程。

表 3　本文式(8)和 Martins-Cardoso-Barcia 方程对三元非电解质水溶液体系的推算结果

Table 3　Estimation results of this work eq. (8) and Martins-Cardoso-Barcia equation for viscosity of ternary aqueous non-electrolyte solutions

Systems	N_D	T/K	This work eq. (8)		Martins-Cardoso-Barcia eq. (1)		Ref.
			AAD / %	Max*AD* / %	*AAD* / %	Max*AD* / %	
Water(1) / Methanol(2) / Ethanol(3)	116	283-323	6.61	23.28	11.71	41.30	[14]
Water(1) / Methanol(2) / 1-Propanol(3)	24	303.15	0.81	0.92	2.02	13.46	[14]
Water(1) /Ethanol(2) / 1-Propanol(3)	24	303.15	1.62	1.81	2.77	11.24	[14]
Water(1) / Methanol(2) / Acetone(3)	28	298.15	3.85	4.43	7.44	16.58	[47]
Water(1) / 2-Propanol(2) / DAA (3)	36	323.15	6.05	6.80	11.39	21.74	[48]
Water(1) /1,4-Dioxane (2) / DMSO(3)	58	303-313	3.56	13.14	15.37	36.07	[4]
Water(1) / DMF(2) / NMF (3)	66	298.15	3.77	5.40	14.17	14.40	[49]
Total *AAD* / %			3.75		14.93		

4 结 论

本文将形状因子引入到 Fang 和 He 提出的非水液体混合物黏度方程中，提出了一个非电解质水溶液的黏度计算方法，并利用该方法对包括了水 / 醇、水 / 醇醚、水 / 胺、水 / 醇胺、水 / 酰胺、水 / 羧酸、水 / 腈、水 / 吡咯烷酮、水 / 亚砜、水 / 哌啶和水 / 吡咯烷的 54 个二元非电解质水溶液体系的黏度(总计 2876 个黏度数据点)进行了关联，关联的总平均相对偏差分别为 4.60%；对 7 个三元非电解质水溶液体系的黏度(总计 352 个黏度数据点)进行了推算，推算的总平均相对偏差分别为 3.75%。与较有代表性的 Martins-Cardoso-Barcia 黏度方程相比，本文方法对二元非电解质水溶液黏度具有较高的关联精度，对三元非电解质水溶液黏度具有较高的推算精度，具有较好的实用价值。

符号说明：

AAD — 平均相对偏差
f — 形状因子
Max*AD* — 最大偏差
N — 液体混合物组分数
N_A — 阿伏伽德罗常数
N_D — 数据点数
N_{Sys} — 体系数
q — UNIQUAC面积参数
R — 气体常数，8.314 J·mol^{-1}·K^{-1}
S — 摩尔面积，cm^2·mol^{-1}
Total *AAD* — 总平均相对偏差
T — 绝对温度，K
u — UNIQUAC作用参数，J·mol^{-1}
V — 摩尔体积，cm^3·mol^{-1}
x — 摩尔分数
β — 对比形状因子
η — 动力黏度，mPa·s
θ — 表面积分数
λ — UNIQUAC面积分数
π — 圆周率
Φ — UNIQUAC体积分数
χ — 二元能量作用参数，J·cm^{-2}
Ψ — 二元能量作用参数，J·cm^{-2}

上、下标

cal — 计算值
exp — 实验值
mix — 混合物
* — 非电解质水溶液
i — 组分 *i*
j — 组分 *j*
W — 水

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非电解质水溶液黏度的关联

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