Ion–Solvent Interactions in Water-rich Binary Mixtures. Viscometric Behaviour of Sodium Salt Solutions in Water + Sulpholane Mixtures at 30, 40 and 50 °C

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The relative viscosities of NaCl, NaBr, NaI and NaClO$_4$ have been measured at 30, 40 and 50 °C in water + sulpholane mixtures, in the water-rich region. The resulting Jones–Dole *B* coefficients and their dependence on temperature provide useful information as regards changes in water structure when small amount of organic cosolvent is added. The results are also discussed in terms of the transition-state treatment.

Numerous studies have shown that viscosity measurements are very useful in providing information regarding ion–solvent interactions and particularly as regards the modifications induced by ions on the solvent structure. The viscometric technique has generally been used in studying the behaviour of electrolytes in pure solvents,[1-10] while little research has been carried out on electrolytic solutions in mixed solvents.[11-13]

We decided to study systematically the viscometric properties of a number of electrolytes dissolved in binary water + organic-solvent mixtures in the water-rich region, since we believe such investigations can provide useful information on the effects induced by the cosolvent on the water structure.

In the present study viscometric measurements are given for NaCl, NaBr, NaI and NaClO$_4$ in water + sulpholane mixtures in mole fractions of sulpholane [X(sulpholane)] equal to 0.0208, 0.0744 and 0.1586 at 30, 40 and 50 °C.

EXPERIMENTAL

The apparatus and the experimental technique used for viscometric and densimetric measurements have been described elsewhere.[3, 8] The estimated precision of the measured viscosity data was always better than 0.05%.

NaCl, NaBr, NaI were ultrapure grade (Merck). These salts, after drying, were used without further purification.

NaClO$_4$ (Fisher reagent grade) was recrystallized several times from water + methanol mixtures and dried at 150 °C in a vacuum oven for 4 days.

The purification of water and sulpholane has been described previously.[14]

RESULTS

For the calculation of the *B* coefficients by means of the Jones–Dole equation[15] [eqn (1)]

$$\eta_r = 1 + Ac^{\frac{1}{2}} + Bc \tag{1}$$

we followed the method based on the principle of orthogonal polynomials suggested by Vincent *et al.*,[16] who have studied in detail the effects on the *B* coefficient of

higher-order concentration terms in 'extended' Jones–Dole equations. We note at this point that in order to achieve the highest possible degree of uniformity among the viscometric data, it is advisable to use only one method for calculating B coefficients, and we feel that the method suggested by Vincent *et al.* is the most suitable for this purpose.

In order to determine the B coefficients we always used the theoretical value of the A coefficients obtained by means of eqn (2)[17]

$$A = \frac{0.2577 \, \Lambda_0}{\eta_0 (\varepsilon T)^{\frac{1}{2}} \lambda_0^+ \lambda_0^-} \left[1 - 0.6863 \left(\frac{\lambda_0^+ - \lambda_0^-}{\Lambda_0} \right)^2 \right]. \tag{2}$$

The conductometric data and the values of the physical properties of the solvent mixtures were taken from a previous study of ours.[14] Note that the viscometric calculations were carried out at the same percentages of solvent mixtures used in measuring conductances in order to be able to use the values of limiting equivalent conductances. Moreover, since it was not possible to obtain limiting conductance values of ions at temperatures other than 30 °C, we assumed that the A coefficients did not vary significantly with temperature; therefore the same A coefficients used at 30 °C were also used at 40 and 50 °C.

TABLE 1.—THEORETICAL A COEFFICIENTS IN WATER + SULPHOLANE MIXTURES AT 30 °C

	$A/\mathrm{dm}^{\frac{3}{2}} \, \mathrm{mol}^{-\frac{1}{2}}$			
X(sulpholane)	NaCl	NaBr	NaI	NaClO$_4$
0.0208	0.0062	0.0062	0.0063	0.0068
0.0744	0.0062	0.0062	0.0066	0.0073
0.1586	0.0064	0.0062	0.0066	0.0073

In table 1 the A values used in the calculation are reported. The experimental results for NaCl, NaBr, NaI an NaClO$_4$ in the water + sulpholane mixtures at the three temperatures are reported in the Appendix in table 6. The calculated B coefficients at 30, 40 and 50 °C are reported in table 2.

On applying transition state treatment to the relative viscosity of electrolytic solutions[12] an equation can be obtained from which it is possible to calculate the molar free energy of activation of the solution for viscous flow:

$$B = \frac{\overline{V}_1^\circ - \overline{V}_2^\circ}{1000} + \frac{\overline{V}_1^\circ}{1000} \frac{(\Delta\mu_2^{\circ\neq} - \Delta\mu_1^{\circ\neq})}{RT} \tag{3}$$

where $\Delta\mu_1^{\circ\neq}$, the molar free energy of activation of the pure solvent, can be obtained by means of eqn (4):

$$\Delta\mu_1^{\circ\neq} = RT \ln \left(\frac{\eta_0 \overline{V}_1^\circ}{hN} \right) \tag{4}$$

and $\overline{V}_1^\circ$ and $\overline{V}_2^\circ$ are the partial molar volumes of the solvent and solute, respectively. In order to calculate the molar volume of the solvent we treated each solvent mixture as a pure material, and thus obtained $\overline{V}_1^\circ$ by means of eqn (5):

$$\overline{V}_1^\circ = \frac{X_1 M_1 + X_2 M_2}{d}. \tag{5}$$

The values of the partial molar volumes of the electrolyte, $\bar{V}_2^{\,\circ}$, in solvent mixtures at different temperatures were calculated by means of precise density measurements.*

Moreover, by measuring the B coefficients at different temperatures the enthalpies and entropies of activation can be obtained by means of the equations

$$\left. \begin{array}{l} \Delta \bar{S}_2^{\circ \neq} = -\mathrm{d}(\Delta \mu_2^{\circ \neq})/\mathrm{d}T \\ \Delta \bar{H}_2^{\circ \neq} = \Delta \mu_2^{\circ \neq} + T \Delta \bar{S}_2^{\circ \neq}. \end{array} \right\} \tag{6}$$

The values of the activation parameters of the solvent and solutes are reported in tables 3 and 4, respectively.

TABLE 2.—VISCOSITY $B/\mathrm{dm}^3\ \mathrm{mol}^{-1}$ COEFFICIENTS IN WATER + SULPHOLANE MIXTURES AT 30, 40 AND 50 °C

	30 °C	40 °C	50 °C
	X(sulpholane) = 0^a		
NaCl	0.088 ± 0.001	0.099 ± 0.002	0.109 ± 0.002
NaBr	0.058 ± 0.001	0.069 ± 0.001	0.084 ± 0.002
NaI	0.014 ± 0.001	0.033 ± 0.001	0.048 ± 0.001
NaClO$_4$	0.022 ± 0.001	0.044 ± 0.001	0.060 ± 0.001
	X(sulpholane) = 0.0208		
NaCl	0.105 ± 0.001	0.111 ± 0.001	0.121 ± 0.001
NaBr	0.076 ± 0.001	0.094 ± 0.001	0.107 ± 0.002
NaI	0.029 ± 0.001	0.048 ± 0.001	0.060 ± 0.001
NaClO$_4$	0.041 ± 0.002	0.055 ± 0.001	0.063 ± 0.001
	X(sulpholane) = 0.0744		
NaCl	0.177 ± 0.001	0.167 ± 0.002	0.162 ± 0.002
NaBr	0.152 ± 0.002	0.162 ± 0.002	0.168 ± 0.001
NaI	0.113 ± 0.001	0.128 ± 0.002	0.139 ± 0.002
NaClO$_4$	0.107 ± 0.002	0.111 ± 0.002	0.126 ± 0.002
	X(sulpholane) = 0.1586		
NaCl	0.285 ± 0.001	0.276 ± 0.001	0.267 ± 0.001
NaBr	0.253 ± 0.001	0.253 ± 0.003	0.250 ± 0.003
NaI	0.205 ± 0.002	0.209 ± 0.002	0.215 ± 0.003
NaClO$_4$	0.186 ± 0.003	0.186 ± 0.002	0.180 ± 0.001

^{a} From ref. (8).

TABLE 3.—SOLVENT ACTIVATION PARAMETERS

X(sulpholane)	$\Delta H_{1,313}^{\circ \neq}$ /kJ mol^{-1}	$313\ \Delta S_1^{\circ \neq}$ /kJ mol^{-1}	$\Delta \mu_{1,303}^{\circ \neq}$ /kJ mol^{-1}	$\Delta \mu_{1,313}^{\circ \neq}$ /kJ mol^{-1}	$\Delta \mu_{1,323}^{\circ \neq}$ /kJ mol^{-1}
0^a	14.78	5.95	9.04	8.83	8.66
0.0208	15.21	5.79	9.62	9.42	9.25
0.0744	15.74	5.01	10.91	10.73	10.59
0.1586	16.38	4.07	12.46	12.31	12.20

^{a} From ref. (8).

* The $\bar{V}_2^{\,\circ}$ values of the salts will be reported and discussed in a later paper.

TABLE 4.—SOLUTE ACTIVATION PARAMETERS AT 40 °C

salt	X(sulpholane)	$\Delta\mu_{2,313}^{\circ\neq}$ /kJ mol^{-1}	$313\,\Delta S_2^{\circ\neq}$ /kJ mol^{-1}	$\Delta H_{2,313}^{\circ\neq}$ /kJ mol^{-1}
NaCl	0.0208	23.8	-40.7	-16.9
	0.0744	28.4	12.5	40.9
	0.1586	35.3	17.2	52.5
NaBr	0.0208	22.6	-70.4	-47.8
	0.0744	28.0	-26.6	1.4
	0.1586	33.3	-7.8	25.5
NaI	0.0208	18.3	-64.2	-45.9
	0.0744	26.2	-50.1	-23.9
	0.1586	30.8	-23.5	7.3
NaClO$_4$	0.0208	20.3	-56.4	-36.1
	0.0744	25.6	-42.3	-16.7
	0.1586	29.6	0.3	29.9

DISCUSSION

The behaviour of electrolytes in water + sulpholane mixtures in water-rich regions can first be analysed by observing their B and dB/dT coefficients. In pure water it is well-known that the Na$^+$ ion has a low B value;[1] moreover, we have recently shown[8] that its differential dB/dT, while not being virtually zero as had been thought,[1] is only slightly influenced by a variation in temperature between 30 and 50 °C. Therefore we can state that the noteworthy positive values shown by dB/dT for NaCl, NaBr, NaI and NaClO$_4$ salts in pure water are due exclusively to the anion. For this reason all the anions that we have taken into consideration are defined as 'structure breakers' in pure water. On the other hand, the behaviour of the Na$^+$ ion and of Cl$^-$, Br$^-$, I$^-$ and ClO$_4^-$ ions in pure sulpholane is completely different.[3] In fact, the high value of the B coefficient found for Na$^+$ ion, with $dB/dT < 0$, shows that it is strongly solvated in sulpholane and behaves as a 'structure maker'. In contrast in the case of anions, the low B coefficient values, with $dB/dT \approx 0$, show that they interact weakly with the solvent molecules. On the basis of the behaviour of the ions in water and in sulpholane, the noticeable increase in B observed for all salts as the percentage of sulpholane is increased in the mixtures (table 2) can be explained by supposing that interactions between the Na$^+$-sulpholane molecules become more and more important. Let us now consider the dependence of B on temperature (table 5). Up to mole fraction 0.0208 all salts show a positive dB/dT value, and the same applies in pure water, although the values are smaller. When the mole fraction rises to 0.0744, while NaCl shows a small negative dB/dT value, the dB/dT values for the other salts are still positive, although smaller when compared with the values at X(sulpholane) = 0.0208. Lastly, at X(sulpholane) = 0.1586, while dB/dT for NaCl is appreciably less than zero, NaBr and NaClO$_4$ have $dB/dT \approx 0$, and only NaI still shows a low positive value of dB/dT. This behaviour can be explained if one bears in mind that the structure-breaking ability of the anions generally increases with increasing size of the ion, and if one supposes that sulpholane acts as a breaker of water structure. Thus as the percentage of sulpholane in the solvent increases, the anions become less effective structure breakers. It can thus be understood how the dB/dT coefficients, which are

A. SACCO, G. PETRELLA, A. DELL'ATTI AND A. DE GIGLIO   1511

positive for all the salts in pure water and X(sulpholane) $= 0.0208$, change their sign at higher mole fractions of sulpholane and how this happens for the more able structure-breaking anions only in mixtures richer in sulpholane. The hypothesis that sulpholane has hydrophilic properties is also proved by the results of studies on water + sulpholane mixtures carried out using various experimental methods.[18-21]

The analysis of the solute activation parameters reported in table 4 shows that in the region $0 \leqslant X$(sulpholane) $\leqslant 0.0208$ both $\Delta H_2^{\circ\neq}$ and $\Delta S_2^{\circ\neq}$ are negative for all

TABLE 5.—dB/dT COEFFICIENTS IN WATER + SULPHOLANE MIXTURES IN THE RANGE 30-50 °C

	(dB/dT)/dm³ mol⁻¹ K⁻¹			
X(sulpholane)	NaCl	NaBr	NaI	NaClO₄
0[a]	0.001 05	0.001 30	0.001 70	0.001 90
0.0208	0.000 80	0.001 55	0.001 55	0.001 10
0.0744	0.000 75	0.000 80	0.001 30	0.000 95
0.1586	− 0.000 90	− 0.000 15	0.000 50	− 0.000 30

[a] From ref. (8).

salts; this fact indicates that, in this range, the average transition state is associated with bond making and an increase in order. On the other hand, with an increase in the percentage of sulpholane in the mixtures, the values of $\Delta H_2^{\circ\neq}$ and $\Delta S_2^{\circ\neq}$ are increasingly less negative, and in some cases they are both positive at X(sulpholane) $= 0.1586$. In the latter cases and with the highest concentrations of sulpholane we can suppose that the transition state for viscous flow is accompanied by the breaking and distortion of intermolecular bonds.

Moreover, the smooth progression of the values of electrolyte activation parameters found in the water + sulpholane mixtures (table 4) confirms the absence of structural enhancement of the water by the sulpholane; in fact when the water structure is increased by the addition of a cosolvent, maxima or minima in the values of activation parameters of viscous flow are obtained, as can be seen for electrolytes in water + methanol[12] and water + acetone[22] mixtures.

In order to be able to discuss more fully the behaviour of electrolytes it would undoubtedly be useful to know the ionic values of the B coefficients in the solvent mixtures; nevertheless, we feel that it is possible to conclude that the viscometric behaviour of suitably chosen electrolytes can provide information as regards the effect caused by small additions of organic solvents on the structure of water.

Lastly, note that in the above discussion the solvent mixtures are treated as average pure solvents. Obviously this does not allow us to point out the possible occurrence of preferential solvation of one of the components of the mixture toward the ions.

APPENDIX

TABLE 6.—CONCENTRATION, c/mol dm^{-3}, RELATIVE DENSITY, d_r, AND RELATIVE VISCOSITY, η_r, FOR NaCl, NaBr, NaI AND NaClO$_4$ IN WATER + SULPHOLANE MIXTURES AT 30, 40 AND 50 °C. MEASUREMENTS NOT INCLUDED IN THE CALCULATION OF THE B VALUES ARE MARKED WITH AN ASTERISK.

c	d_r	η_r	c	d_r	η_r	c	d_r	η_r
	30 °C			40 °C			50 °C	
			X(sulpholane) = 0.0208					
			NaCl					
0.015 948	1.000 65	1.002 38	0.015 879	1.000 66	1.002 55	0.015 801	1.000 70	1.002 70
0.030 041	1.001 18	1.004 15	0.029 911	1.001 21	1.004 32	0.029 763	1.001 24	1.004 66
0.036 611	1.001 44	1.004 95	0.036 451	1.001 42	1.005 02	0.036 273	1.001 51	1.005 60
0.051 526	1.002 02	1.006 68	0.051 302	1.002 05	1.007 05	0.051 049	1.002 06	1.007 83
0.068 716	1.002 71	1.008 82	0.068 416	1.002 70	1.009 32	0.068 079	1.002 73	1.010 01
0.083 613	1.003 25	1.010 70	0.083 253	1.003 30	1.011 14	0.082 838	1.003 26	1.011 60
			NaBr					
0.018 574	1.001 43	1.002 25	0.018 494	1.001 40	1.002 52	0.018 402	1.001 48	1.002 98
0.027 863	1.002 11	1.003 00	0.027 742	1.002 10	1.003 67	0.027 605	1.002 16	1.004 05
0.033 745	1.002 56	1.003 61	0.033 598	1.002 53	1.004 28	0.033 433	1.002 64	1.004 94
0.046 294	1.003 50	1.004 75	0.046 093	1.003 49	1.005 55	0.045 866	1.003 58	1.006 35
0.064 374	1.004 87	1.006 61	0.064 093	1.004 83	1.007 64	0.063 777	1.004 90	1.008 30
0.077 613	1.005 87	1.007 56	0.077 273	1.005 82	1.008 95	0.076 889	1.005 87	1.009 82
			NaI					
0.012 711	1.001 38	1.001 07	0.012 656	1.001 40	1.001 29	0.012 594	1.001 42	1.001 47
0.020 166	1.002 21	1.001 47	0.020 079	1.002 22	1.001 83	0.019 980	1.002 24	1.002 03
0.024 727	1.002 70	1.001 78	0.024 619	1.002 70	1.002 14	0.024 498	1.002 73	1.002 40
0.034 071	1.003 73	1.002 19	0.033 924	1.003 77	1.002 89	0.033 756	1.003 77	1.003 23
0.047 181	1.005 16	1.002 73	0.046 975	1.005 15	1.003 61	0.046 742	1.005 16	1.004 15
0.056 141	1.006 11	1.003 10	0.055 894	1.006 05	1.004 15	0.055 625	1.006 19	1.004 85
			NaClO$_4$					
0.014 730	1.001 07	1.001 35	0.014 667	1.001 08	1.001 64	0.014 595	1.001 08	1.001 71
0.021 158	1.001 54	1.001 52	0.021 066	1.001 55	1.002 18	0.020 963	1.001 56	1.002 23
0.026 178	1.001 92	1.002 20	0.026 065	1.001 92	1.002 55	0.025 937	1.001 92	1.002 63
0.038 193	1.002 80	1.002 88	0.038 026	1.002 77	1.003 54	0.037 837	1.002 74	1.003 82
0.052 644	1.003 84	1.003 78	0.052 414	1.003 80	1.004 29	0.052 154	1.003 77	1.004 81
0.064 471	1.004 75	1.004 52	0.064 187	1.004 68	1.005 35	0.063 867	1.004 61	1.005 79
			X(sulpholane) = 0.0744					
			NaCl					
0.017 728	1.000 69	1.003 98	0.017 628	1.000 75	1.003 66	0.017 523	1.000 88	1.003 31
0.029 836	1.001 11	1.006 06	0.029 666	1.001 13	1.005 86	0.029 488	1.001 23	1.005 71
0.034 899	1.001 29	1.007 21	0.034 700	1.001 30	1.006 78	0.034 491	1.001 39	1.006 64
0.047 854	1.001 77	1.009 89	0.047 579	1.001 73	1.009 00	0.047 293	1.001 82	1.008 87
0.071 724	1.002 62	1.014 52	0.071 314	1.002 62	1.013 63	0.070 888	1.002 75	1.013 08
0.080 971	1.003 05	1.016 11	0.080 504	1.002 99	1.015 46	0.080 016	1.003 03	1.014 99
			NaBr					
0.021 357	1.001 45	1.004 02	0.021 236	1.001 36	1.004 36	0.021 107	1.001 36	1.004 35
0.030 279	1.002 11	1.005 57	0.030 106	1.002 02	1.005 83	0.029 924	1.002 04	1.005 94
0.036 170	1.002 53	1.006 35	0.035 963	1.002 42	1.006 70	0.035 744	1.002 39	1.006 95
0.050 344	1.003 57	1.009 34	0.050 055	1.003 45	1.009 70	0.049 754	1.003 51	1.009 76
0.068 827	1.004 87	1.012 11	0.068 439	1.004 85	1.012 74	0.068 026	1.004 88	1.013 03
0.083 501	1.006 13	1.014 45	0.083 028	1.006 07	1.015 36	0.082 551	1.006 42	1.015 88
			NaI					
0.012 991	1.001 38	1.002 23	0.012 917	1.001 42	1.002 03	0.012 838	1.001 41	1.003 15
0.020 251	1.002 05	1.003 22	0.020 135	1.002 05	1.003 26	0.020 014	1.002 09	1.003 66
0.025 591	1.002 66	1.004 00	0.025 444	1.002 66	1.004 42	0.025 290	1.002 70	1.004 63
0.033 956	1.003 51	1.005 22	0.033 761	1.003 50	1.005 75	0.033 557	1.003 52	1.005 75
0.047 484	1.004 88	1.006 75	0.047 212	1.004 87	1.007 64	0.046 937	1.005 13	1.008 28
0.057 304	1.005 86	1.008 02	0.056 977	1.005 90	1.008 42	0.056 628	1.005 83	1.008 92

TABLE 6.—(*continued*)

c	d_r	η_r	c	d_r	η_r	c	d_r	η_r
	30 °C			40 °C			50 °C	
				X(sulpholane) = 0.0744				
				NaClO$_4$				
0.014 056	1.000 88	1.002 54	0.013 976	1.000 86	1.002 52	0.013 893	1.000 99	1.002 80
0.022 348	1.001 38	1.003 41	0.022 221	1.001 38	1.003 44	0.022 088	1.001 49	1.003 90
0.026 048	1.001 65	1.004 12	0.025 900	1.001 62	1.004 28	0.025 745	1.001 74	1.004 45
0.035 979	1.002 22	1.005 51	0.035 775	1.002 25	1.005 36	0.035 564	1.002 41	1.006 03
0.049 742	1.003 16	1.006 94	0.049 457	1.003 14	1.006 85	0.049 163	1.003 26	1.007 61
0.059 997	1.003 90	1.007 93	0.059 653	1.003 86	1.008 48	0.059 296	1.003 94	1.009 27
				X(sulpholane) = 0.1586				
				NaCl				
0.011 436	1.000 72	1.004 02	0.011 361	1.000 81	1.003 74	0.011 283	1.000 86	1.003 60
0.018 985	1.000 97	1.006 37	0.018 862	1.001 11	1.006 06	0.018 730	1.001 08	1.005 83
0.032 986	1.001 41	1.010 61	0.032 767	1.001 45	1.010 28	0.032 544	1.001 57	1.009 81
0.045 083	1.001 68	1.014 42	0.044 790	1.001 84	1.013 74	0.044 481	1.001 88	1.013 15
0.049 400	1.001 78	1.015 43	0.049 078	1.001 92	1.015 21	0.048 739	1.001 93	1.014 54
0.072 926	1.002 55	1.022 32	0.072 442	1.002 58	1.021 50	*0.071 943	1.002 61	1.020 15
				NaBr				
0.019 201	1.000 90	1.005 80	—	—	—	—	—	—
0.026 431	1.001 25	1.007 81	0.026 256	1.001 53	1.007 67	0.026 079	1.001 48	1.007 57
0.034 284	1.001 77	1.009 81	0.034 057	1.002 05	1.009 88	0.033 832	1.002 11	1.009 41
0.045 723	1.002 54	1.012 75	0.045 423	1.002 86	1.012 90	0.045 132	1.003 14	1.012 86
0.063 164	1.003 83	1.017 63	0.062 748	1.004 14	1.017 96	0.062 328	1.004 11	1.017 00
*0.075 746	1.004 57	1.020 10	0.075 247	1.004 87	1.020 17	*0.074 741	1.004 82	1.019 68
				NaI				
0.019 075	1.001 85	1.005 13	0.018 951	1.001 96	1.004 97	0.018 823	1.002 05	1.004 99
0.031 242	1.002 84	1.007 79	0.031 038	1.002 91	1.007 91	0.030 830	1.003 07	1.007 97
0.035 646	1.003 54	1.008 75	0.035 413	1.003 62	1.008 81	0.035 174	1.003 70	1.009 01
0.048 005	1.004 62	1.011 51	0.047 690	1.004 67	1.011 79	0.047 370	1.004 83	1.012 24
0.065 419	1.006 26	1.014 90	0.064 982	1.006 34	1.015 05	0.064 551	1.006 55	1.015 36
0.080 557	1.007 67	1.018 29	0.080 033	1.007 79	1.018 37	0.079 492	1.007 88	1.018 62
				NaClO$_4$				
0.016 113	1.000 81	1.004 05	0.016 006	1.000 72	1.004 21	0.015 896	1.000 55	1.003 98
0.023 018	1.001 23	1.005 78	0.022 870	1.001 30	1.005 27	0.022 710	1.000 98	1.005 16
0.030 201	1.001 66	1.007 16	0.030 001	1.001 55	1.006 91	0.029 797	1.001 44	1.006 77
0.040 035	1.002 25	1.009 09	0.039 770	1.002 16	1.008 81	0.039 496	1.001 95	1.008 32
0.055 314	1.003 13	1.011 87	0.054 956	1.003 16	1.011 88	0.054 578	1.002 98	1.011 44
0.067 617	1.003 91	1.014 25	0.067 182	1.004 00	1.014 34	0.066 711	1.003 67	1.013 97

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