Supplementary Materials

Competitive Adsorption of Ionic Liquids Versus Friction Modifier and Anti-wear Additive at Solid/Lubricant Interface—Speciation with Vibrational Sum Frequency Generation Spectroscopy

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Fittings of SFG spectra

SFG spectra in the current study were fitted using the Lorentzian line shape described in the following equation [1].

$$I_{SFG} = \left| \sum_m \frac{A_m}{\omega_m - \omega_{IR} + i\Gamma_m} + ne^{-i\varepsilon} \right|^2$$

In the above equation, for an m^{th} resonant mode, A_m, ω_m, and Γ_m are the oscillator strength) wavenumber (vibrational frequency), and line width (damping constant), respectively. ω_{IR} is the tuning IR wavenumber. The parameters n and ε are the amplitude and phase of non-resonant background, respectively. The Curve Fitting Tool in MATLAB was used for the spectral deconvolution. The fitting results are given in Tables S1–6.

Table S1. Fitting results of *SSP* spectra of single compounds at solid/liquid interface. A_m, ω_m, and Γ_m are the amplitude, wavenumber, and damping constant, respectively, of the m^{th} resonant mode. A ≡ DEHP

Sample	A_1	ω_1 (cm^{-1})	Γ_1 (cm^{-1})	A_2	ω_2 (cm^{-1})	Γ_2 (cm^{-1})	A_3	ω_3 (cm^{-1})	Γ_3 (cm^{-1})	A_4	ω_4 (cm^{-1})	Γ_4 (cm^{-1})	A_5	ω_5 (cm^{-1})	Γ_5 (cm^{-1})
PAO4	1.85	2855	5.00	4.23	2869	8.38	3.11	2911	10.93	6.12	2925	10.64	7.11	2942	10.05
[N888H][A]	1.04	2849	5.00	2.51	2873	5.24	5.44	2904	23.61	-	-	-	12.39	2943	14.15
[P8888][A]	1.61	2847	5.43	2.41	2873	6.20	2.88	2915	11.06	-	-	-	12.89	2941	14.12
OFM	-	-	-	2.45	2885	8.91	5.17	2902	11.84	3.19	2920	12.65	11.61	2949	14.74
Sec-ZDDP	-	-	-	1.13	2874	5.37	1.66	2895	12.93	0.96	2921	8.20	14.60	2947	18.18

Table S2. Fitting results of *PPP* spectra of single compounds at solid/liquid interface. A_m, ω_m, and Γ_m are the amplitude, wavenumber, and damping constant, respectively, of the m^{th} resonant mode. A ≡ DEHP

Sample	A_1	ω_1 (cm^{-1})	Γ_1 (cm^{-1})	A_2	ω_2 (cm^{-1})	Γ_2 (cm^{-1})	A_3	ω_3 (cm^{-1})	Γ_3 (cm^{-1})	A_4	ω_4 (cm^{-1})	Γ_4 (cm^{-1})	A_5	ω_5 (cm^{-1})	Γ_5 (cm^{-1})
PAO4	-	-	-	0.65	2878	4.00	1.21	2897	5.00	2.38	2915	8.17	6.57	2960	7.32
[N888H][A]	0.89	2844	6.87	1.56	2871	6.59	-	-	-	0.14	2922	5.00	4.37	2941	11.00
[P8888][A]	0.84	2849	3.10	1.84	2872	5.00	-	-	-	-	-	-	12.26	2941	12.33
OFM	-	-	-	2.22	2879	10.69				5.93	2950	10.87	1.14	2963	3.38
Sec-ZDDP	-	-	-	1.05	2870	8.24							6.92	2947	11.42

Table S3. Fitting results of *SSP* spectra of two compound mixtures at silica/liquid interface. A_m, ω_m, and Γ_m are the amplitude, wavenumber, and damping constant, respectively, of the m^{th} resonant mode. A ≡ DEHP

Sample	A_1	ω_1 (cm^{-1})	Γ_1 (cm^{-1})	A_2	ω_2 (cm^{-1})	Γ_2 (cm^{-1})	A_3	ω_3 (cm^{-1})	Γ_3 (cm^{-1})	A_4	ω_4 (cm^{-1})	Γ_4 (cm^{-1})	A_5	ω_5 (cm^{-1})	Γ_5 (cm^{-1})
PAO4 + [N888H][A]	-	-	-	2.10	2877	5.29	3.80	2891	10.52	5.61	2913	11.14	9.11	2943	11.12
PAO4 + [P8888][A]	1.00	2844	3.00	4.04	2873	7.23	6.62	2914	12.35	-	-	-	10.18	2941	12.21
PAO4 + OFM	-	-	-	0.90	2889	6.98	2.54	2901	9.64	9.61	2916	17.60	10.56	2951	13.61
PAO4 + sec-ZDDP	3.03	2861	9.30	-	-	-	2.23	2899	13.09	1.38	2917	5	15.54	2946	15.00
PAO4 + PIBSI	2.67	2852	7.08	4.35	2871	8.84	-	-	-	15.57	2925	13.84	5.42	2956	10.65

Table S4. Fitting results of *PPP* spectra of two compound mixtures at silica/liquid interface. A_m, ω_m, and Γ_m are the amplitude, wavenumber, and damping constant, respectively, of the m^{th} resonant mode. A ≡ DEHP

Sample	A_1	ω_1 (cm^{-1})	Γ_1 (cm^{-1})	A_2	ω_2 (cm^{-1})	Γ_2 (cm^{-1})	A_3	ω_3 (cm^{-1})	Γ_3 (cm^{-1})	A_4	ω_4 (cm^{-1})	Γ_4 (cm^{-1})	A_5	ω_5 (cm^{-1})	Γ_5 (cm^{-1})
PAO4 + [N888H][A]	0.52	2849	3.00	3.19	2874	6.82	-	-	-	-	-	-	13.54	2942	13.79
PAO4 + [P8888][A]	0.47	2844	2.00	2.50	2873	5.83	-	-	-	-	-	-	13.38	2943	13.13
PAO4 + OFM	-	-	-	9.325	2895	22.5	-	-	-	5.19	2952	10.64	3.27	2965	4.00
PAO4 + sec-ZDDP	0.39	2864	3.00	-	-	-	-	-	-	12.03	2942	16.49	7.65	2973	9.67
PAO4 + PIBSI	-	-	-	-	-	-	-	--	-	22.84	2930	13.95	-	-	-

Table S5. Fitting results of *SSP* spectra of three compound mixtures at silica/liquid interface. A_m, ω_m, and Γ_m are the amplitude, wavenumber, and damping constant, respectively, of the m^{th} resonant mode. A ≡ DEHP

Sample	A_1	ω_1 (cm^{-1})	Γ_1 (cm^{-1})	A_2	ω_2 (cm^{-1})	Γ_2 (cm^{-1})	A_3	ω_3 (cm^{-1})	Γ_3 (cm^{-1})	A_4	ω_4 (cm^{-1})	Γ_4 (cm^{-1})	A_5	ω_5 (cm^{-1})	Γ_5 (cm^{-1})
PAO4 + OFM + [N888H][A]	-	-	-	1.16	2881	5.37	4.21	2894	11.86	8.84	2915	15.42	6.99	2947	11.29
PAO4 + OFM + [P8888][A]	0.79	2845	3.00	4.18	2876	9.00	-	-	-	7.20	2915	13.68	10.82	2942	13.44
PAO4 + PIBSI + [N888H][A]	-	-	-	3.88	2895	12.42	-	-	-	11.51	2917	12.87	10.44	2948	12.32
PAO4 + PIBSI + [P8888][A]	1.29	2848	7.35	-	-	-	-	-	-	11.00	2920	13.27	6.61	2954	11.49
PAO4 + ZDDP + [N888H][A]	-	-	-	5.59	2882	13.13	-	-	-	7.89	2911	13.95	8.47	2943	11.26
PAO4 + ZDDP + [P8888][A]	0.26	2848	4.00	1.38	2875	4.87	-	-	-	5.20	2916	9.78	13.25	2944	14.05

Table S6. Fitting results of *PPP* spectra of three compound mixtures at silica/liquid interface. A_m, ω_m, and Γ_m are the amplitude, wavenumber, and damping constant, respectively, of the m^{th} resonant mode. A ≡ DEHP

Sample	A_1	ω_1 (cm^{-1})	Γ_1 (cm^{-1})	A_2	ω_2 (cm^{-1})	Γ_2 (cm^{-1})	A_3	ω_3 (cm^{-1})	Γ_3 (cm^{-1})	A_4	ω_4 (cm^{-1})	Γ_4 (cm^{-1})	A_5	ω_5 (cm^{-1})	Γ_5 (cm^{-1})
PAO4 + OFM + [N888H][A]	-	-	-	-	-	-	-	-	-	-	-	-	9.73	2951	13.87
PAO4 + OFM + [P8888][A]	0.69	2849	3.00	2.16	2873	4.59	-	-	-	-	-	-	14.22	2944	14.32
PAO4 + PIBSI + [N888H][A]	2.18	2869	6.90	-	-	-	-	-	-	-	-	-	6.50	2942	11.29
PAO4 + PIBSI + [P8888][A]	-	-	-	-	-	-	-	-	-	3.71	2922	9.36	2.71	2940	5.47
PAO4 + ZDDP + [N888H][A]	-	-	-	1.50	2873	7.19	-	-	-	-	-	-	9.35	2943	1.80
PAO4 + ZDDP + [P8888][A]	-	-	-	0.71	2873	3.37	-	-	-	-	-	-	10.69	2943	13.52

References

1. Ngo, D.; Liu, H.; Chen, Z.; Kaya, H.; Zimudzi, T.J.; Gin, S.; Mahadevan, T.; Du, J.; Kim, S.H. Hydrogen bonding interactions of H2O and SiOH on a boroaluminosilicate glass corroded in aqueous solution. *npj Materials Degradation* **2020**, *4*, 1, doi:10.1038/s41529-019-0105-2.