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A Measure of the Electron-donating Power and Electron-accepting Power of Liquid Organic Compounds

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A quantitative study has been made of the measurement of the electron-donating nature and the electron-accepting nature of various liquid organic compounds. The position of the O–D or C=O absorption band of a liquid compound which contained a small quantity of methanol-d or of acetophenone was measured by means of an infrared spectrophotometer. The relative magnitude of the electron-donating nature or of the electron-accepting nature of the compound was compared by a measurement of the perturbation which it produced on the O–D vibrational band of methanol-d or on the C=O vibrational band of acetophenone. The electron-donating power or the electron-accepting power of a compound is defined as the relative difference (counted as wave numbers) of the O–D or the C=O absorption band observed in the compound from that in benzene. From the results, it was found that, in a homologous series, the electron-donating power decreased with an increase in the ionization potential in the gaseous phase, or with an increase in the pK_b value in the liquid phase, and that it increased linearly with the co-ordination power to diethyl zinc. It was also found that the electron-accepting power increased with an increase in the electron affinity in the gaseous phase and decreased with an increase in the pK_a value in the liquid phase. Moreover, the various liquid organic compounds, classified into four typical groups, were considered on the basis of their electron-donating and electron-accepting power.

It has previously been reported[1,2] that the solvent effect in ionic polymerization was dependent on the relative magnitude of the electron-donating power or on that of the electron-accepting power of the monomer and solvent used.

On the other hand, Gordy *et al.* have made a study of the proton-attracting properties of various liquid compounds,[3] while the relative acceptor strengths of some inorganic halides have been reported on by Lappert *et al.*[4]

The purpose of this report was to evaluate the relative magnitude of the electron-donating nature or the electron-accepting nature of various liquid organic compounds on the basis of the infrared spectral data. The O–D or the C=O vibrational band of the compounds containing a small amount of methanol-d or acetophenone were measured by means of an infrared spectrophotometer. On the basis of these data, a measure of the electron-donating power and of the electron-accepting power of liquid organic compounds was proposed.

Experimental

Materials. The aromatic and aliphatic hydrocarbons, esters, ethers, nitriles, amines, ketones, aldehydes, amides, imines, lactones, sulfoxides, nitro compounds, and inorganic halides were all obtained commercially and were purified by the usual method. Methanol-d, bp 64.5—65.0°C; acetophenone, bp 202°C/750 mmHg.

Apparatus and Method. The infrared spectra of the O–D band of methanol-d or of the C=O band of acetophenone in the mixture were determined with a Hitachi EPI-2 infrared spectrophotometer (resolving power: 3 cm^{-1} at 10 μ; slit width: 0.03 mm at 10 μ), equipped with a sodium chloride prism; the cell used was 0.010 cm, thick. A small quantity of methanol-d or acetophenone was added to a solution of 1.0 m*l* of the liquid organic compound in a 2.0 m*l* weighing bottle. The concentration of acetophenone was 0.1 mol/*l* while that of methanol-d was 0.4 mol/*l*, because the position of the O–D vibrational band was not clear when the concentration of methanol-d was lower than 0.4 mol/*l*. After having been shaken for 10 min at room temperature (18 ± 3°C), the mixture was used for the measurement of the infrared spectrum. The error in the measured shifts of the O–D band is not more than ±1 cm^{-1}, whereas that of the C=O band is ±0.3 cm^{-1} (with the scale up). The electronic properties of various liquid organic compounds were then compared by a measurement of the different perturbations which they caused in the O–D vibrational band of methanol-d or in the C=O vibrational band of acetophenone in the mixture.

Results and Discussion

The positions of the monomeric O–D and C=O vibrational bands of various liquid organic compounds are listed in Table 1, together with the

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[1] A. V. Tobolsky and C. E. Rogers, *J. Polymer Sci.*, **38**, 205 (1959).

[2] Yu Spirin, A. A. Arest-Yakubovich, D. K. Polyakov and S. S. Mendrev, *ibid.*, **58**, 1181 (1962).

[3] W. Gordy and S. C. Stanford, *J. Chem. Phys.*, **9**, 204 (1941).

[4] M. F. Lappert, *J. Chem. Soc.*, **1962**, 542.

TABLE 1. ELECTRON-DONATING POWERS AND ELECTRON-ACCEPTING POWERS OF LIQUID ORGANIC COMPOUND

No.	Compound	Position of O-D band ν_D (cm^{-1})	Electron-donating power $\Delta\nu_D$ (cm^{-1})	Position of C=O band ν_A (cm^{-1})	Electron-accepting power $\Delta\nu_A$ (cm^{-1})
	Aromatic hydrocarbons and derivatives				
1	Benzene	2668	0	1690.2	0
2	Toluene	2666	2	1691.1	−0.9
3	Ethylbenzene	2664	4		
4	Styrene	2666	2	1689.2	1.0
5	α-Methylstyrene	2664	4		
6	*p*-Methylstyrene	2666	2		
7	Chlorobenzene	2670	−2	1689.3	0.9
8	Bromobenzene	2669	−1	1689.5	0.7
9	*o*-Dichlorobenzene	2679	−11	1687.4	2.8
10	*m*-Dichlorobenzene	2683	−15	1688.5	1.7
	Aliphatic hydrocarbons and derivatives				
11	*n*-Hexane	2667	1		
12	*n*-Heptane	2668	0		
13	Carbon tetrachloride	2689	−21	1691.0	−0.8
14	Chloroform	2685	−17		
15	Methylene chloride	2680	−12		
16	Ethylene chloride	2666	2		
	Nitro compounds				
17	Nitromethane	2662	6	1685.4	4.8
18	Nitroethane	2660	8	1686.6	3.6
19	Nitrobenzene	2647	21	1681.2	9.0
	Nitriles				
20	Acetonitrile	2619	49	1688.3	1.9
21	Propionitrile	2616	52		
22	Acrylonitrile	2631	37	1688.0	2.2
23	Benzonitrile	2630	38		
	Esters				
24	Methyl acetate	2632	36		
25	Ethyl acetate	2629	39		
26	Methyl chloroacetate	2641	27		
27	Methyl dichloroacetate	2645	23		
28	Methyl propionate	2635	33		
29	Ethyl propionate	2636	32		
30	Methyl isobutyrate	2636	32		
31	Vinyl acetate	2647	21		
32	Methyl acrylate	2638	30		
33	Ethyl acrylate	2635	33		
34	Methyl metacrylate	2631	37		
	Lactones				
35	β-Propiolactone	2634	34		
36	γ-Butyrolactone	2602	66		
37	ε-Caprolactone	2586	82		
	Ketones				
38	Acetone	2604	64		
39	Methyl ethyl ketone	2611	57		
40	Diethyl ketone	2612	56		
41	Methyl vinyl ketone	2579	89		
42	Cyclohexanone	2602	66		

TABLE 1 (Continued)

No.	Compound	Position of O-D band ν_D (cm^{-1})	Electron-donating power $\Delta\nu_D$ (cm^{-1})	Position of C=O band ν_A (cm^{-1})	Electron-accepting power $\Delta\nu_A$ (cm^{-1})
43	Acetophenone	2612	56		
	Ethers				
44	Diethyl ether	2590	78	1693.6	−3.4
45	Di-*n*-propyl ether	2595	73		
46	Diisopropyl ether	2593	75	1694.2	−4.0
47	Ethyl *n*-butyl ether	2591	77	1693.5	−3.3
48	Ethyl vinyl ether	2637	31	1690.4	−0.2
49	*n*-Butyl vinyl ether	2635	33		
50	Isobutyl vinyl ether	2635	33		
51	Diallyl ether	2602	66		
52	1,2-Dimethoxyethane	2597	71	1691.7	−1.5
53	Anisole	2642	26	1688.8	1.4
54	Phenetole	2643	25		
55	Propylene oxide	2609	59	1690.8	−0.6
56	Epichlorohydrin	2623	45	1687.0	3.2
57	Styrene oxide	2617	51		
58	3,3-Bischloromethyloxetane	2590	78	1689.0	0.8
59	Furan	2664	4		
60	Tetrahydrofuran	2578	90	1690.0	0.2
61	1,3-Dioxolane	2610	58		
62	2-Methyl-1,3-dioxolane	2607	61		
63	4-Methyl-1,3-dioxolane	2612	56		
64	2-Phenyl-1,3-dioxolane	2612	56		
65	4-Chloromethyl-1, 3-dioxolane	2625	43		
66	Tetrahydropyran	2575	93	1696.1	−5.9
67	1,4-Dioxane	2591	77	1690.0	0.2
	Aldehydes				
68	Acetaldehyde	2589	79		
69	Propionaldehyde	2583	85		
70	*n*-Butyraldehyde	2585	83		
71	Acrolein	2546	122		
72	Crotonaldehyde	2593	75		
73	Benzaldehyde	2615	53		
	Amines				
74	Ethylamine	2435	233		
75	*n*-Propylamine	2438	230		
76	Di-*n*-propylamine	2426	242		
77	Triethylamine	2430	238	1695.0	−4.8
78	Aniline	2510	158		
79	*N*-Methylaniline	2517	151		
80	*N*, *N*-Dimethylaniline	2520	148		
81	Pyridine	2500	168		
82	α-Picoline	2485	183		
83	γ-Picoline	2508	160		
84	4-Ethylpyridine	2489	179		
85	*o*-Toluidine	2523	145		
86	Piperidine	2428	240		
87	4-Vinylpyridine	2475	193		
	Imines				
88	Ethylenimine	2431	237		
89	*N*-Phenylethylenimine	2482	186		

TABLE 1. (continued)

No.	Compound	Position of O–D band ν_{D} (cm^{-1})	Electron-donating power $\Delta\nu_{\mathrm{D}}$ (cm^{-1})	Position of C=O band ν_{A} (cm^{-1})	Electron-accepting power $\Delta\nu_{\mathrm{A}}$ (cm^{-1})
	Amides				
90	*N,N*-Dimethylformamide	2561	107		
91	*N,N*-Dimethylacetamide	2555	113		
	Sulfoxides				
92	Dimethyl sulfoxide	2527	141	1682.0	8.2
	Inorganic Halides				
93	Zinc chloride			1618.0	72.2
94	Tin chloride			1582.0	108.2
95	Antimony pentachloride			1565.0	125.2

chemical structures of the compounds. The positions of the O–D vibrational band vary from about 2400 to 2700 cm^{-1} with the kind of compound, and the Lewis bases, such as the ethers and amines, shift to lower frequencies because of the formation of hydrogen bonds. In the C=O band, on the other hand, the Lewis acids which form the coordination bonds with another atom having an electron-pair cause a greater shift to a lower frequency.

Electron-donating Power and Electron-accepting Power. It is considered that the electron-donating nature of liquid compounds corresponds to the proton-attracting force and that the electron-accepting nature is the electron-pair-attracting force. On the basis of the considerations described above, we propose that the electron-donating power or the electron-accepting power of a liquid organic compound is to be defined as the relative difference (counted as wave numbers) of the O–D or the C=O absorption band observed in the compound from that in benzene, chosen as a reference compound.

Electron-donating Power:

$$\Delta\nu_{\mathrm{D}}=\nu_{\mathrm{D}}(\text{benzene})-\nu_{\mathrm{D}}(\text{compound})$$

Electron-accepting Power:

$$\Delta\nu_{\mathrm{A}}=\nu_{\mathrm{A}}(\text{benzene})-\nu_{\mathrm{A}}(\text{compound})$$

From the above definition, it can be said that the greater the $\Delta\nu_{\mathrm{D}}$ or the $\Delta\nu_{\mathrm{A}}$ value, the stronger is the proton-attracting force or the electron-pair-attracting force.

Examination of $\Delta\nu_{\mathrm{D}}$ Values. The $\Delta\nu_{\mathrm{D}}$ as defined above expresses the electron-donating power in the state of aggregation. On the other hand, since the ionization potential is the smallest energy which is necessary for taking a valence electron from a gaseous atom or molecule, it is reasonable to consider that the ionization potential is related to the electron-donating power. The relation between the $\Delta\nu_{\mathrm{D}}$ values of several typical liquids and the ionization potentials[5,6] in the gaseous phase is shown in Fig. 1. That the $\Delta\nu_{\mathrm{D}}$ values decreased with an increase in the ionization potentials was observed in any homologous series of aliphatic and aromatic hydrocarbons, ethers, esters, or ketones.

A regular relationship was also observed between the $\Delta\nu_{\mathrm{D}}$ and pK_b values[7] of various aliphatic

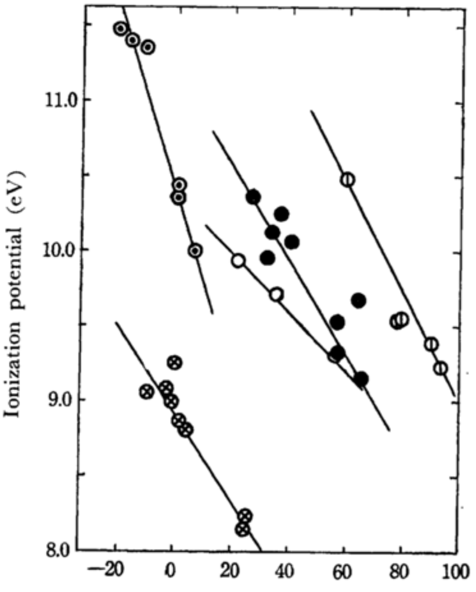

Fig. 1. Relation between the ionization potentials and the electron-donating powers ($\Delta\nu_{\mathrm{D}}$) of various organic compounds.
⊗ Unconjugated aromatic compounds
○ Conjugated aromatic compounds
⊙ Aliphatic compounds
● Esters and ketones
⦶ Ethers

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[5] K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).
[6] F. I. Vipesov and B. P. Kurbatov, *Dokl. Akad. Nauk, SSSR*, **140**, 1364 (1961).
[7] N. F. Hall and M. R. Sprinkle, *J. Am. Chem. Soc.*, **54**, 3469 (1932).

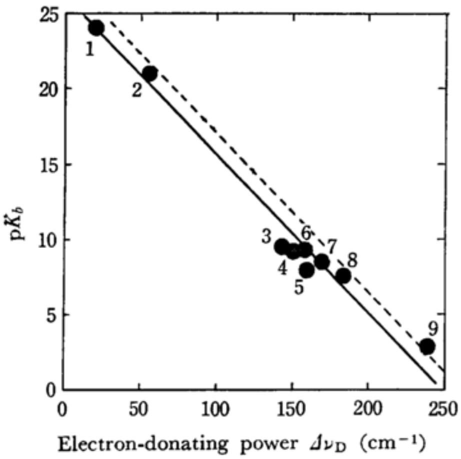

Fig. 2. Relation between the pK_b values of various aromatic and aliphatic amines and the electron-donating powers ($\Delta\nu_D$).

--- Gordy work $pK_b = -0.102\Delta\nu_D + 26.8$
—— Present work $pK_b = -0.102\Delta\nu_D + 26.3$
1 Nitrobenzene, 2 Acetophenone, 3 *o*-Toluidine
4 Methylaniline, 5 γ-Picoline, 6 Aniline,
7 Pyridine, 8 α-Picoline, 9 Triethylamine

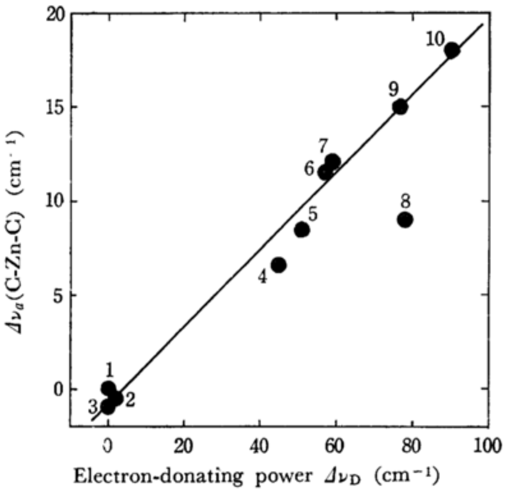

Fig. 3. Relation between the co-ordination powers to diethyl zinc and the electron donating powers.

1 Benzene, 2 Toluene, 3 *n*-Heptane,
4 Epichlorohydrin, 5 Styrene oxide,
6 Ethylene oxide, 7 Propylene oxide,
8 Diethyl ether, 9 Dioxane,
10 Tetrahydrofuran

and aromatic amines. Figure 2 shows that the larger the $\Delta\nu_D$ value is, the smaller is the pK_b value of the liquid organic compound.

On the other hand, Ishimori and Tsuruta have spectrally investigated the co-ordination power of cyclic ethers to diethyl zinc, which is regarded as an electrophilic compound.[8] It may be inferred that the ether having the stronger co-ordination power to diethyl zinc has the larger electron-donating power. Figure 3 shows that the co-ordination power to diethyl zinc increases linearly with the $\Delta\nu_D$ value.

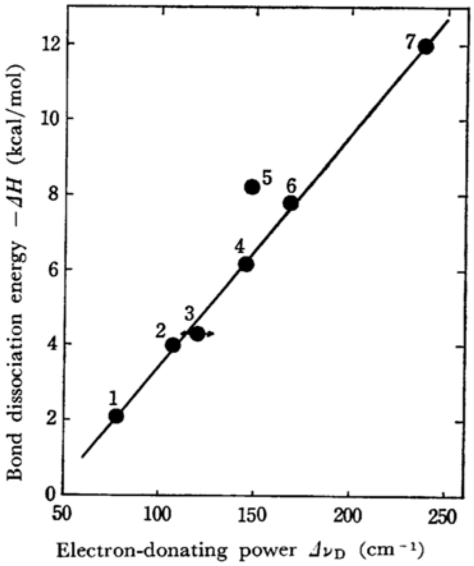

Fig. 4. Relation between the bond dissociation energies of the charge transfer complexes (I_2–electron donors) and the electron donating powers ($\Delta\nu_D$) of the electron donors.

1 Diethyl ether, 2 *N, N*-Dimethylformamide,
3 Ethanol, 4 *o*-Toluidine,
5 *N, N*-Dimethylaniline, 6 Pyridine,
7 Triethylamine

Moreover, since it is considered that the hydrogen bond formed between the methanol-d molecule and the solvent molecule is due to the charge transfer, the $\Delta\nu_D$ value may be expected to be related to the bond dissociation energy of the charge-transfer complex[9] formed between the iode molecule and the electron-donor molecule. In order to discuss this relation, we tried to plot the $\Delta\nu_D$ values of the electron donors against the bond dissociation energies of the charge-transfer complexes. As Fig. 4 shows, the energies of the bond dissociation of the charge-transfer complexes are in better correlation with the $\Delta\nu_D$ values than with the ionization potentials.

From these results, it may be concluded that the $\Delta\nu_D$ value expresses quantitatively the electron-donating power in both the gaseous and liquid phases.

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[8] M. Ishimori and T. Tsuruta, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **70**, 378 (1967).

[9] P. A. D. de Maine, *J. Chem. Phys.*, **26**, 1192 (1957); C. Reid and R. S. Mulliken, *J. Am. Chem. Soc.*, **76**, 3869 (1954); S. Nagakura, *ibid.*, **80**, 520 (1958); H. Tsubomura, *ibid.*, **82**, 40 (1960); H. Tsubomura and R. P. Lang, *ibid.*, **83**, 2085 (1961).

Examination of $\Delta\nu_A$ Values. The $\Delta\nu_A$ value of liquid compound is defined above as the electron-accepting power in the state of aggregation. On the other hand, the electron affinity of a compound is defined as the energy generated when its molecule absorbs an electron; this has been regarded as a measure of the electron-accepting power in the gaseous phase. Scarcely no experimental values of the electron affinities have, however, been reported. In order to evaluate the electron affinity, the energy ($\varepsilon_{lv}=\alpha-\eta_{lv}\beta$, α, $\beta<0$) of the lowest unoccupied σ level was used, since it is reasonable to consider that the smaller the coefficient (η_{lv}) of β in the energy of the lowest unoccupied level, the greater is the electron affinity, *i.e.*, the electron-accepting power of the compound in the gaseous phase. Figure 5 shows that the $\Delta\nu_A$ values decrease with an increase in the η_{lv} values.[10]

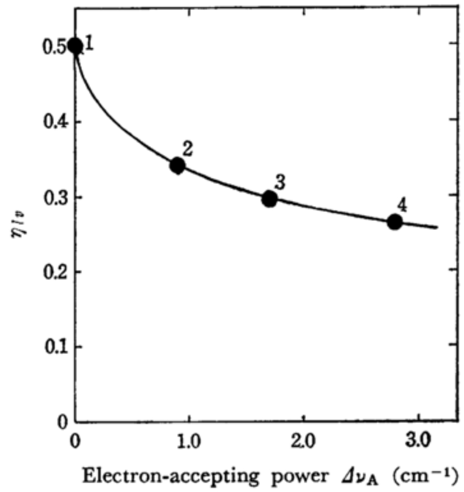

Fig. 5. Relation between the energies of the lowest unoccupied σ level and the electron-accepting powers ($\Delta\nu_A$) of aromatic halides.

$\varepsilon_{lv}=\alpha-\eta_{lv}\beta$. 1 Benzene, 2 Chlorobenzene, 3 *m*-Dichlorobenzene, 4 *o*-Dichlorobenzene

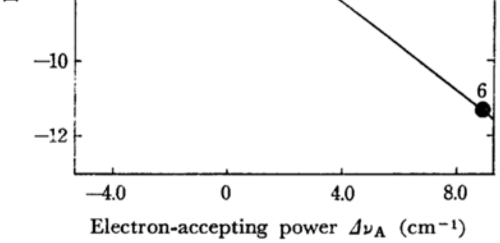

Fig. 6. Relation between the pK_a values of various ethers and the electron-accepting power ($\Delta\nu_A$).

1 Tetrahydropyran, 2 Diisopropyl ether,
3 *n*-Butyl ethyl ether, 4 Di-*n*-butyl ether,
5 Anisole, 6 Nitrobenzene

On the other hand, a linear relation was found to exist between the $\Delta\nu_A$ values and the pK_a values[11] of various ethers and aromatic compounds, as is shown in Fig. 6. The $\Delta\nu_A$ values of liquid compounds decrease with an increase in the pK_a values.

From these results, it may be concluded that the $\Delta\nu_A$ values express quantitatively the electron-accepting power in both the gaseous and liquid phases.

A Consideration of Liquid Organic Compounds on the Basis of the Electron-donating Power and the Electron-accepting Power. It is well known that Lewis bases like the ethers employed in the Grignard reaction and in the S_N2 reaction are the nucleophilic solvents, that the nitro compounds employed in the Friedel-Crafts reaction and Lewis acids are electrophilic solvents, and that the hydrocarbons have scarcely no ionization power. From these facts, the liquid organic compounds have been classified qualitatively into the following four groups: (1) amphoteric liquids,

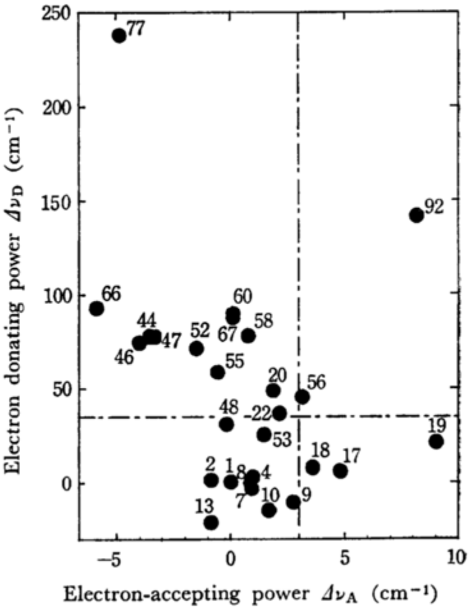

Fig. 7. Relation between the electoron-donating power ($\Delta\nu_D$) and the electron-accepting power ($\Delta\nu_A$) of various liquid organic compounds. The number of a point represents the number in Table 1.

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[10] K. Fukui, K. Morokuma, H. Kato and T. Yonezawa, This Bulletin, **36**, 217 (1963).

[11] E. M. Arnett and C. Y. Wu, *J. Am. Chem. Soc.*, **84**, 1684 (1962).

(2) nucleophilic liquids, (3) electrophilic liquids and (4) non-philic liquids.

Little attention has, however, been paid to the quantitative consideration of the liquid compounds on the basis of the electronic features, in spite of the importance of this approach. In Fig. 7 we have plotted the relation between the $\Delta\nu_D$ values and the $\Delta\nu_A$ values of various liquid organic compounds. As Fig. 7 shows, the electron-donating power is more dominant than the electron-accepting power in most liquid organic compounds. In view of the classification on the basis of the results shown in Fig. 7, it is reasonable to take a point, with a $\Delta\nu_D$ value of 35 cm^{-1} and a $\Delta\nu_A$ value of 3 cm^{-1} as the standard point. In the amphoteric liquids the $\Delta\nu_D$ and $\Delta\nu_A$ values are both larger than the standard point, while, in the non-philic liquids both are smaller. The nucleophilic liquids have larger $\Delta\nu_D$ values and smaller $\Delta\nu_A$ values, while the electrophilic liquids have smaller $\Delta\nu_D$ values and larger $\Delta\nu_A$ values than the standard point. This quantitative classification, based on the electronic features of liquid organic compounds, seems useful as an unifying interpretation for many kinds of experimental results.

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