

Analysis of the Flow Patterns of Liquid Organic Compounds between Blade Electrodes by Classification Models

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The flow patterns of 20 organic liquids with diverse structures and functionalities between electrodes were measured under a dc electric field. The results clearly showed the existence of a strong relationship between the flow pattern of a compound and its molecular structure. On the basis of a variety of 23 molecular descriptors including those obtained by quantum-chemical calculations, multiple regression analysis and discriminant analysis were applied to identify the significant factors contributing to the flow patterns. For the flow rate dipole moment, nucleophilic delocalizability and lipophilicity as expressed by the 1-octanol/water partition coefficient were found to be the key factors as judged by a five-value regression model with a squared correlation coefficient (r^2) of 0.881. For the direction of the flow, just two quantum-chemical parameters, namely, absolute hardness and the self-polarizability normalized by molecular volume, were identified as significant factors by using linear discriminant analysis. The numbers of misclassified compounds were only one and two for training and prediction (leave-one-out cross-validation), respectively, by the best discriminant model.

INTRODUCTION

The directional crystallization method has been developed to purify organic chemicals.^{1–3} In a previous work⁴ the effect of a dc electric field on the purification of 3,5-xyleneol (95 wt %) + naphthalene (5 wt %) mixtures during solidification was examined experimentally. In the experiment, liquid flow between electrodes was observed through the microscope with a video camera and the liquid phase was highly agitated. As a result, the concentration of naphthalene used as an impurity could be decreased in the solid phase. This fact may be attributable to the turbulence in the liquid phase caused by the applied electric field. Thus, the impurity near the solid–liquid interface can be removed by the liquid flow. In practice, to develop the application of an electric field to the solidification processes as a new method of purification, an understanding of the quantitative relationship between chemical structure or physicochemical properties and the flow behavior of organic compounds is required.

Only a few studies related to similar phenomena have been reported until now. Sumoto⁵ first observed experimentally a rising effect of dielectric liquids, such as chloroform and xylene, along with high-voltage electrodes. The Sumoto effect was further investigated using several kinds of electrode materials and dielectric liquids.⁶ Watanabe⁷ ex-

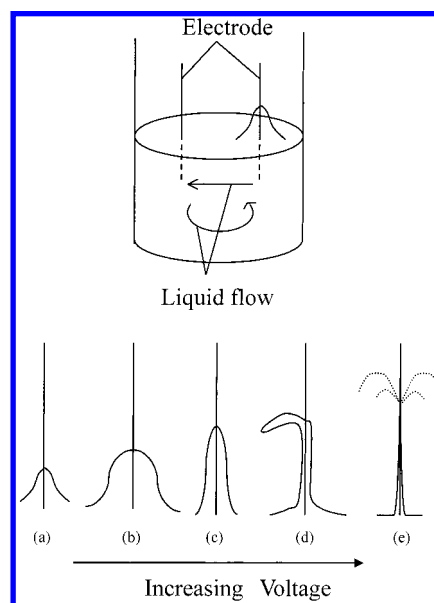


Figure 1. Observed typical patterns of the rising behavior of liquids along with a high-voltage electrode.⁷

plored the rising behavior of a series of 15 liquids including aliphatic hydrocarbons, halogenated hydrocarbons, esters, and ketones along with a high-voltage electrode. As shown in Figure 1, five typical patterns of the rising liquid were observed with an increase of the voltage. For nonpolar liquids, only pattern a could be seen. Patterns c and d were mainly observable for halogenated hydrocarbons and ketones. In the case of ketones, in addition pattern e was obtained.

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Table 1. Organic Liquids Tested and Observed Data for Liquid Flow between Electrodes

compd no.	compd	purity (%)	supplier	temp (°C)	flow rate ^g L	direction of flow (-, +)
1	acetone	≥99.5	Tokyo ^d	40	4	←
2	benzene	≥99.5	Wako ^e	40	0	—
3	benzoic acid ^a	≥99.5	Wako	130	2	→
4	bromobenzene	≥99.0	Tokyo	40–100	1	→
5	butyronitrile	≥99.0	Tokyo	40	4	←
6	cyclohexane	≥99.5	Wako	40	0	—
7	cyclopentanone	≥99.0	Tokyo	40	4	←
8	dibutylamine	≥99.0	Tokyo	40	3	←
9	dibutyl ether	≥99.0	Tokyo	40	2	←
10	3,5-dimethyl phenol ^b	≥99.0	Tokyo	70	3	→
11	ethanol	≥99.5	Wako	40	3	→
12	hexane	≥96.0	Wako	40	0	—
13	isobutyraldehyde	≥95.0	Tokyo	40	3	←
14	naphthalene ^c	≥99.0	Nacalai ^f	87	2	←
15	nitrobenzene	≥99.5	Wako	40	3	←
16	<i>o</i> -xylene	≥98.0	Tokyo	40–100	1	←
17	phenyl acetate	≥98.0	Tokyo	40	3	←
18	quinoline	≥98.0	Tokyo	40	3	←
19	sulfolane	≥99.0	Tokyo	40	3	→
20	thiophene	≥98.0	Tokyo	40	1	→

^a mp = 122 °C. ^b mp = 68 °C. ^c mp = 81 °C. ^d Tokyo Kasei Kogyo Co., Ltd., Tokyo, Japan. ^e Wako Pure Chemical Industries, Ltd., Osaka, Japan. ^f Nacalai Tesque, Inc., Kyoto, Japan. ^g Observed by the naked eye: class 0, no flow; class 1, low; class 2, medium; class 3, high; class 4, very high.

Therefore, the observed rising effect was closely related to the chemical structure of the investigated compounds, and according to Watanabe, the effect was influenced by an attractive electrostatic force. The force exerted on the electrode was found to be proportional to the dielectric constants of the liquids. Furthermore, when certain kinds of dielectric liquids were tested under the application of a dc voltage, it was found that the liquid was pumped up continuously (see Figure 1). The author explained such a liquid flow by the assumption that molecules solvated around positive or negative charges are attracted to the anode or cathode, respectively. For example, acetone molecules contain electronegative oxygen atoms which are easily solvated around the positive charge and are attracted to the cathode, suggesting that there is a qualitative relationship between the liquid flow and the applied electric field.

The aim of this study was to explore the flow patterns of 20 liquid organic compounds by observing their flow rates and the direction of the liquid flow under a constant electric field. Our preliminary study revealed that the flow patterns could not be expressed as a simple function of the dielectric constants or dipole moments of the liquids, so multiple regression analysis and discriminant analysis⁸ have been applied to identify the significant molecular properties contributing to the flow patterns of liquids. It is expected that such approaches will be highly useful for this problem, which cannot be readily analyzed by a rigid theoretical treatment.

MATERIALS AND METHODS

Test Chemicals. The 20 organic compounds used are listed in Table 1 together with their purities, suppliers, and measurement temperatures. The selection of these compounds was based on their structure and functionality to be repre-

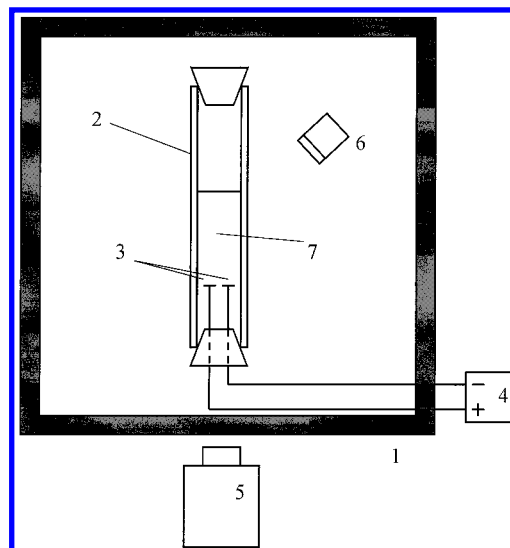


Figure 2. Structure of the apparatus: (1) air bath; (2) glass tube; (3) blade electrodes; (4) dc power supply; (5) video camera; (6) light; (7) liquid sample.

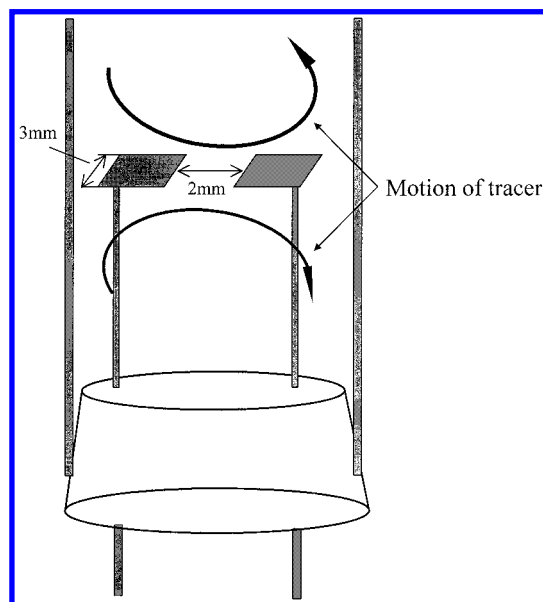


Figure 3. Enlarged schematic of the electrodes ((3) in Figure 2).

sentative of some typical classes of organic molecules. They include six saturated, aromatic, and halogenated hydrocarbons and eight oxygen-, four nitrogen-, and two sulfur-containing compounds.

Apparatus and Procedure. The schematic diagrams of the apparatus and electrodes used are shown in Figures 2 and 3, respectively. A glass tube with an inner diameter of 17.6 mm was put into an air bath. Stainless steel blade electrodes were set inside the glass tube. The distance between the edges of two electrodes was 2 mm. A liquid sample containing chalk powder used as tracer was placed in the tube. The sample was allowed to remain in the air bath for 1 h to allow the temperature to stabilize. Generally, the experiment was performed at 40 °C as shown in the fifth column in Table 1, except for the three compounds, **3**, **10**, and **14**, with higher melting points. For these three molecules the air bath was regulated at a temperature above their melting points. In addition, to check for a possible dependence of the flow on the temperature for the two compounds

4 and **16**, their flows were measured at 40, 60, 80, and 100 °C. A dc electric field of 400 V was applied by an electrophoresis power supply (Atto Corp., AE-3132, Tokyo, Japan). The flow patterns between the electrodes were visible with the unaided eye through a microscope with a video camera (see Figure 3). A light was fixed in the air bath to allow the flow patterns to be clearly observed.

Physicochemical Characterization Parameters. The charge distribution of a molecule in an external electric field is distorted, resulting in a relative displacement of the positive and negative atomic charges. The resulting induced dipole moment in the molecule and other polarity-related properties are expected to be the critical factors affecting the flow of organic liquids between blade electrodes. Therefore, the results of quantum-chemical calculations were used as a basis for the physicochemical characterization of the test compounds. In addition to electronic properties, geometrical properties were also calculated since it has been shown that for quantitative structure–chromatographic retention relationships such descriptors were found to be of key importance for molecular transport.⁹ Apart from the quantum-chemical parameters, molecular connectivity indices¹⁰ $^0\chi$ and $^1\chi$, molar refraction MR, dielectric constant ϵ , molecular polarizability¹¹ α_0 , molar magnetic susceptibility χ_M , and 1-octanol/water partition coefficient $\log K_{ow}$ have also been used to describe some electronic and geometrical aspects of the molecules. For the calculations of MR and α_0 , the ChemProp system¹² was used.

The molecular orbital calculations were performed with the two program packages MOPAC 93¹³ and VAMP¹⁴ using the AM1¹⁵ Hamiltonian. Geometries were completely optimized with the aid of the eigenvector-following routine. Descriptors of the electronic structure calculated by these methods include dipole moments μ (experimental values were also collected), energies of the highest occupied orbital (ϵ_{HOMO}) and lowest virtual orbital (ϵ_{LUMO}), and atomic charges obtained by Mulliken population analysis (charges Q_m^+ and Q_m^- of the most positive and negative atoms, respectively, as well as relative positive (Q_r^+) and negative (Q_r^-) charges¹⁶). The absolute electronegativity χ ($=-(\epsilon_{HOMO} + \epsilon_{LUMO})/2$) and the absolute hardness η ($=-(\epsilon_{HOMO} - \epsilon_{LUMO})/2$) were evaluated from the HOMO and LUMO energies.¹⁷ χ gives a measure of the electron attraction tendency, and η is interpreted as the resistance of the chemical potential to change when the number of electrons is changed. The nucleophilic and electrophilic delocalizabilities D^N and D^E ¹⁸ are measures for the susceptibility of a molecule to nucleophilic and electrophilic attacks, respectively. The self-polarizability SP characterizes the response of the molecule to local changes in electron energy.¹⁹ For a recent review of these parameters including a specification of the mathematical formulas, the reader is referred to the literature.¹⁹ The geometrical parameters used as descriptors are the molecular surface area SA (\AA^2) and the molecular volume V (\AA^3). The surface area and molecular volume were calculated with the MOLSV program²⁰ using a Monte Carlo integration technique with van der Waals radii often used in continuum solvation models of the MST scheme with geometries optimized in the gas phase.²¹ For SP, values normalized by molecular weight MW and molecular volume V , i.e., SP/MW and SP/ V , were also used since SP increases with molecular size.

Data Analysis Methods. In the present study an attempt has been made to analyze quantitative relationships between the basic physicochemical properties and the behavior of the test molecules in the electric field using discriminant analysis. A description of the calculation procedures for discriminant analysis and its application in chemistry and related fields can be found in numerous publications.²² Therefore, only a brief outline of the methodology is presented here.

Discriminant analysis can be used with classified dependent data. The data may be measured on a nominal scale (yes/no, active/inactive) or an ordinal scale (1, 2, 3; active, medium, inactive). Such category data may also be derived from continuous data by some rule such as “low” if <100 and “high” if >100 . The discriminant function is used to classify the dependent variable (classified data). Among various possible discriminant functions, the following linear or quadratic discriminant functions are used here:

$$Z = a_1X_1 + a_2X_2 + \dots + a_pX_p + a_0 \quad (1)$$

$$Z = a_1X_1 + a_2X_2 + \dots + a_{11}X_1^2 + a_{22}X_2^2 + \dots + a_0 \quad (2)$$

where the X_i are the parameters or the independent variables used to describe the samples, the a_i are fitted coefficients, and a_0 is constant. Where two classes occur, a value of zero for Z may be used as the critical value so that if Z is positive the compound belongs to the first class, if negative then to the second class. For the problem for several classes, the multilinear least-squares regression method was utilized.

RESULTS AND DISCUSSION

Experimental Results. The flow rate and direction of flow caused by the electric field between electrodes are shown in the sixth and seventh columns in Table 1. The data quoted for compounds **4** and **16** are those obtained at 40 °C. Although their viscosities decrease with increasing temperature, there was no temperature dependence of the flow patterns of both liquids within the temperature range of 40–100 °C (the data obtained at temperatures other than 40 °C did not differ from those at 40 °C). From this fact, the data for the three compounds (**3**, **10**, and **14**) that required higher air bath temperatures can be analyzed together with those of all other compounds measured at 40 °C.

The observed flow rates were classified into five scales (Table 1). The scales 4, 3, 2, 1, and 0 denote very high, high, medium, low, and no flow, respectively. For the four compounds benzene, cyclohexane, 3,5-dimethylphenol, and hexane, no flow at all could be seen with the unaided eye. During the experiments no bubbles could be observed near the electrodes.

Analysis of the Flow Rate between Electrodes. The 20 organic compounds contained in this five-class problem were subjected to stepwise regression analysis using the above-mentioned candidates of 23 potentially relevant descriptors: μ (both experimental and calculated values were used), SA, V , ϵ_{HOMO} , ϵ_{LUMO} , χ , η , D^N , D^E , SP, SP/MW, SP/ V , Q_m^+ , Q_m^- , Q_r^+ , Q_r^- , $^0\chi$, $^1\chi$, MR, ϵ , α_0 , χ_M , and $\log K_{ow}$. The selection of descriptors was done on the basis of the following criteria to minimize the possibility of chance correlations: (a) All descriptors with F test values of less than 1 or correlation coefficients with the dependent variable of less than 0.1 were

Table 2. Descriptors Employed for the Analyses of the Flow Rate for 20 Organic Liquids

compd no.	μ_{exptl}^a (D)	$\log K_{\text{ow}}^b$	D^N (eV ⁻¹)	η (eV)	SP/V
1	2.88	-0.24	-2.30	5.76	0.0684
2	0.0	2.13	-3.60	5.10	0.0840
3	1.73	1.87	-4.43	4.81	0.0796
4	1.55	2.99	-3.81	4.83	0.0658
5	3.6	0.60	-2.97	6.66	0.0717
6	0.0	3.44	-4.33	7.30	0.0742
7	3.0	0.31	-3.45	5.69	0.0738
8	1.04	2.83	-7.00	6.21	0.0710
9	1.22	3.21	-6.26	6.64	0.0701
10	1.76	2.35	-5.37	4.68	0.0786
11	1.69	-0.30	-1.96	7.22	0.0394
12	0.08	4.00	-4.54	7.41	0.0703
13	2.58	0.36	-3.00	5.69	0.0694
14	0.0	3.35	-5.91	4.22	0.0887
15	4.22	1.85	-4.25	4.75	0.0810
16	0.62	3.12	-5.04	4.85	0.0810
17	1.91	1.49	-5.45	4.83	0.0798
18	2.18	2.03	-5.60	4.36	0.0884
19	4.81	1.23	-3.25	5.65	0.0663
20	0.55	1.81	-2.96	4.73	0.0743

^a The experimental data were taken from a collection.²⁷ ^b The experimental data were taken from Sangster's data bank.²⁸

excluded from the initial pool of 23 descriptors. (b) All possible combinations of descriptor pairs were examined to identify those pairs which were highly correlated. As a rule of thumb, a value of 0.8^{23,24} for the intercorrelation coefficient was used. If two descriptors were intercorrelated at or above the critical value, one descriptor was discarded.

The best five-value regression equation describing the flow rate was found to be

$$L = 0.374(\pm 0.096)\mu_{\text{exptl}} - 1.00(\pm 0.14) \log K_{\text{ow}} - 0.669(\pm 0.108)D^N + 0.65(\pm 0.31) \quad (3)$$

$$n = 20, r^2 = 0.881, s = 0.4, F = 50.7$$

where L = scored (0–4) flow rate assigned in Table 1, n = number of compounds, r = correlation coefficient, s = standard error, and F = Fisher statistic. The standard error of estimation of each coefficient at the 95% confidence level is given within parentheses. It should be pointed out that this best equation involves only 3 parameters out of the 23 descriptors initially tested.

The relative significance of the descriptors in the above model (eq 3) was in the following order according to the F test: $\log K_{\text{ow}} > D^N > \mu_{\text{exptl}}$. The values of these parameters for the 20 compounds are listed in Table 2. There were no significant pairwise correlations among the three parameters involved in eq 3 (intercorrelation coefficient <0.8). The highest r value between $\log K_{\text{ow}}$ and D^N was -0.711. The results of the classification obtained by this function (eq 3) are shown in Table 3. The ratings of 16 out of the 20 compounds could be classified correctly by eq 3. Thus, the value of the correct classification rate P is 0.8 (=16/20). To check the predictive power and robustness of eq 3, cross-validation or the leave-one-out test was carried out. The prediction by the test provided reasonably good results as can be seen from the data presented in the fourth column in Table 3. Six compounds were misclassified by prediction ($P = 0.7$) as compared to four misclassified compounds by recognition (eq 3). It is very interesting to note that all

Table 3. Classification of Flow Rate Using Multilinear Least-Squares Regression (MLR) and Linear Discriminant Analysis (LDA) for Two Classes

compd no.	MLR			LDA		
	obsd	recg ^a	pred ^b	obsd ^c	recg ^d	pred ^b
1	4	4	3 ^g	1	1	1
2	0	1 ^g	1 ^g	0	0	0
3	2	2	2	0	1 ^g	1 ^g
4	1	1	1	0	0	0
5	4	3 ^g	3 ^g	1	1	1
6	0	0	0	0	0	0
7	4	4	4	1	1	1
8	3	3	3	1	1	1
9	2	2	2	0	0	1 ^g
10	3	3	3	1	1	1
11	3	3	3	1	1	1
12	0	0	0	0	0	0
13	3	3	3	1	1	1
14	2	1 ^g	1 ^g	0	0	0
15	3	3	3	1	1	1
16	1	1	1	0	0	0
17	3	4 ^g	4 ^g	1	1	1
18	3	3	3	1	1	1
19	3	3	4 ^g	1	1	1
20	1	1	1	0	0	0
P^e		0.800	0.700		0.950	0.900
$r^2 f$		0.881	0.822			

^a Rounded values from eq 3. ^b Rounded values from the leave-one-out procedure. ^c 0 = former classes 0, 1, and 2; 1 = former classes 3 and 4. ^d From eq 4. ^e Correct classification rate. ^f r = correlation coefficient. ^g Misclassification.

misclassified cases indicated by footnote g in Table 3 are classified into neighboring groups; none are misclassified by a larger distance. The training success was significantly reduced by exclusion of any one of the parameters $\log K_{\text{ow}}$, D^N , and μ_{exptl} . Furthermore, it can be seen that no single parameter is a statistically significant predictor of the flow rate. The employment of experimental values for μ is somewhat more significant than using the calculated values based on the AM1 method. The use of calculated μ gave $P = 0.750$ and $r^2 = 0.851$ compared to the P and r^2 values shown in Table 3.

The above five-class analysis gave a good correlation; however, it seems that the classification is an overinterpretation of the data since the classification is based on the observation with the naked eye and contains some ambiguities. Therefore, discriminant analysis was applied for two classes, using two potency classes rather than five: class 0 (original classes 0, 1, and 2) and class 1 (original classes 3 and 4). The best result obtained with this approach is also indicated in Table 3. From all possible combinations of linear and quadratic functions for the set of all compounds, the following discriminant function was obtained:

$$Z_1 = -2.45\mu_{\text{exptl}} + 5.44 \log K_{\text{ow}} + 3.41D^N + 7.82 \quad (4)$$

Compounds with a value of Z_1 greater than 0 were classified as class 0, otherwise as class 1. Importantly, the parameters for eq 3 are the same as those included in eq 4. Furthermore, the order of relative significance of the descriptors for class separation was also the same as in the case of eq 3. Therefore, the significance of the three descriptors was verified.

As can be seen from the data collected in the sixth and seventh columns of Table 3 in the case of eq 4 only one (3)

Table 4. Classification of the Direction of Flow Using LDA for Two Classes

compd no.	LDA		
	obsd ^a	recg ^b	pred ^c
1	1	1	1
2			
3	0	1 ^e	1 ^e
4	0	0	0
5	1	1	1
6			
7	1	1	1
8	1	1	1
9	1	1	1
10	0	0	1 ^e
11	0	0	0
12			
13	1	1	1
14	1	1	1
15	1	1	1
16	1	1	1
17	1	1	1
18	1	1	1
19	0	0	0
20	0	0	0
<i>P</i> ^d		0.941	0.882

^a Classification according to the observed direction of flow: class 0, $\rightarrow +$; class 1, $\leftarrow +$. ^b From eq 5. ^c From the leave-one-out procedure. ^d Correct classification rate. ^e Misclassification.

and two molecules (**3** and **9**) were misclassified in the recognition or training ($P = 0.950$) and prediction ($P = 0.900$), respectively. The Z_1 value of compound **3** ($Z_1 = -1.36$) is greater than those of all other compounds in class 1. Since this compound originally was assigned scale 2 in the above five-group classification and very close to scale 3, it is not unexpected that compound **3** is erroneously classified into class 1 here. A similar ambiguity can also be seen in the case of compound **14**.

Much information is hidden in $\log K_{ow}$, probably explaining its successful employment in many quantitative structure–activity relationships (QSARs). Generally speaking, it has been demonstrated that $\log K_{ow}$ is composed of a polarization and an electronic or electrostatic term.^{25,26}

The parameter D^N refers to vacant orbitals only, while SP includes both occupied and vacant orbitals.²⁷ D^N can be interpreted as a measure of H-bonding acidity and can be called acceptor delocalizability (readiness to accept additional electrons).

The energy E of a molecule in the presence of an electromagnetic field of strength F depends on the dipole moment μ and the molecular polarizability α_0 .²⁵ Thus, a correlation between the flow rate and μ or α_0 can be expected. Besides, α_0 can be correlated with D^N , and α_0 is split into a molecular size and an electronic part.²⁶

In view of the above facts it is reasonable to consider that the key factors which govern the flow rate of organic molecules between electrodes are molecular bulk, polarity, polarizability (a measure of the ease with which dipole moments are induced), and H-bonding basicity.

Analysis of the Direction of Flow between Electrodes. According to the experimental observations, the direction of flow was scored as either 0 or 1 for flow from the cathode toward the anode and from the anode toward the cathode, respectively (see the second column in Table 4). Therefore,

a discriminant analysis for two classes was applied. The best discriminant function obtained for the set of all compounds was the following equation:

$$Z_2 = 4.61\eta + 439.2(\text{SP}/V) - 56.4 \quad (5)$$

Notably, only two parameters (see Table 2 for their values; the intercorrelation coefficient between them is -0.784) are involved in this best equation. Compounds with a value of Z_2 greater than 0 were classified as class 1, otherwise as class 0. Application of quadratic discriminant functions using the same set of parameters did not improve the classification rate. Although the coefficient of the SP/V term is much bigger than that of the η term, this merely depends on the original units of the two parameters. In fact, the statistical significances of both parameters in eq 5 for class separation are almost comparable according to the F values of the corresponding coefficients (11.43 and 16.48 for η and SP/V, respectively). Therefore, both terms in eq 5 are equally significant. Only one molecule for training and two molecules for prediction, respectively, are misclassified.

The self-polarizability normalized by volume, SP/V, has been employed to describe chemical reactivity and mainly represents the effect of a perturbation on the electronic charge at one atom. On the other hand, η is defined on the basis of the HOMO–LUMO gap, i.e., the difference in energy between the HOMO and LUMO, and a measure of how easily molecular electron density can be changed. Thus, this parameter is a measure of the general ease of modification of the electronic structure due to an external force. A decrease in the energy gap usually leads to easier polarization of the molecule. From the physical meaning of these two parameters, SP/V and η , it seems that factors related to molecular polarization govern the direction of the flow.

CONCLUSION

The flow pattern data between electrodes were obtained for 20 organic liquids under a dc electric field. Both the flow rate and direction of flow observed showed a significant dependence on the physicochemical properties of the test molecules. Multivariate analyses suggest that a combination of molecular bulk, polarity, polarizability, and H-bonding basicity influences the flow rate, while molecular polarization related factors are the dominant influence on the direction of the flow. These findings can be useful in the development of solidification processes using the electric field.

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