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Demonstration of Electrostatic Field Effect Working on Dipolar Liquids with Correlation to Their Structures

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When an electrically charged body is allowed to come close to a fine water stream falling down from the tip of a capillary, the vertical stream is bent a little towards the charged body by an attractive force due to the electricity-water dipole interaction. We constructed a simple equipment for the purpose of quantitative determination of the attractive force by defining a quantity P to search the correlation between the permittivity ε and the dipole momemt μ of polar liquids. For various pure polar liquids and mixtures at various mole fractions x of the components, we found a proportional correlationship $P\bar{\varepsilon}=k\bar{\mu}$ with a common constant k, when the electric potential applied on an electrode, temperature, and flow velocity are fixed. In the cases of mixtures, $\bar{\varepsilon}=\sum x_i\varepsilon_i$ and $\bar{\mu}=\sum x_i\mu_i$ are used. Pure liquids, such as methanol, ethanol, 1-propanol, acetic acid, acetone, acetonitrile, tetrahydrofuran, 1,4-dioxane, nitromethane, dimethyl sulfoxide, and nitrobenzene and mixtures, such as benzene–ethanol and benzene–nitrobenzene obey the proportionality rule approximately. On the other hand, water and some mixtures such as benzene–acetic acid and benzene–tetrahydrofran fail the rule, suggesting the possibility that molecular association occurs due to their mutual interactions in the liquids. Thus, this method may be considered as a simple demonstration illustrating the states of molecular aggregation in polar liquids.

We often experience a phenomenon even in our daily life that when something electrically charged such as mechanically rubbed plastics is brought close to a fine and smooth water current falling down from an end of a tap, the vertical pillar of water is forced to bend considerably towards the electrically charged body. This is caused by the interaction between the electricity on the charged body and the electric dipoles of water molecules. An idea that this may be caused, instead, by the frictional electricity produced on water surface when it is made to flow down off the end of the tap is easily denied by the facts that the phenomenon is not observed at all if water is replaced by nonpolar liquids such as benzene or 1,4-dioxane and that the interaction force occurs always to be attractive but never repulsive indifferent to whether the sign of the electricity on the rubbed body is positive or negative.

Some effects of electric[1,2] or magnetic[3] fields have ever been found and investigated on the viscosities of water and other several liquids. But the attractive force itself working on polar liquids in electric fields have never been quantitatively measured yet. In the present investigation, we constructed an equipment suitable for quantitative determinations of the forces applied to a variety of dipolar liquids; pure water, some organic substances, their mixtures, and various aqueous solutions of electrolytes. It was necessary to set up a device for reproducing the desired electric fields of constant strength and maintaining the stationary flow of liquids for the purpose. Then, the correlations of the dipole moments of liquids with their permittivities (dielectric constants) will be discussed as a convenient clue for the molecular association in liquids.

Experimental

Equipment. In order to apply a stable and reproducible electric field, a Hamamatsu Regulated DC Power Supply Model HTV-C752 was used as a high voltage source. The electrode of high voltage was made of a copper plate of 2 cm width and 4 cm length. The apparatus for the observation was constructed by wholly connected glass for the use of organic substances, as is shown in Fig. 1. The notations in the figure indicate as follows; A: sample liquid reservoir, B: overflow branch for keeping constant liquid level, C: reservoir bottle for waste liquid, D: capillary tip, E: electrode, F: thermostat, S: high-voltage source, and T: telescope with micrometer. Among the numbered stopcocks 1—6, only cock 1 is of three-way. The electrode and the capillary are settled vertically, and the vertical center line on the electrode surface was arranged to face just in paralled to the liquid current which was steadily flowing down from the end of the capillary tip. The distance between the electrode and the

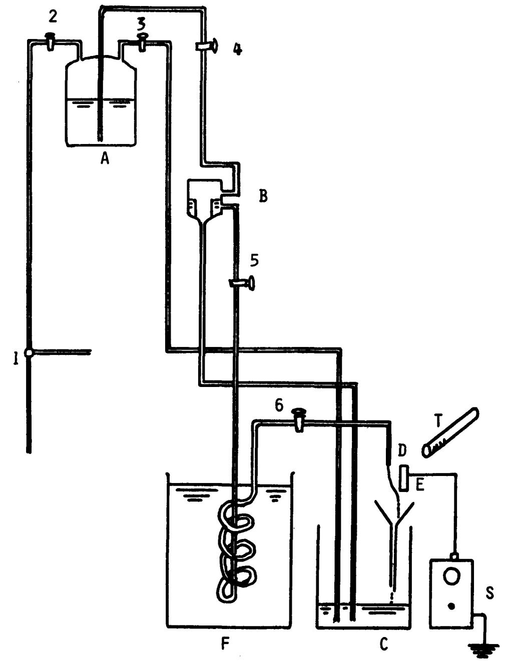


Fig. 1. Glass-connected apparatus for stationary liquid flux.
A: Sample liquid reservoir, B: overflow branch device, C: reservoir bottle for waste liquid, D: capillary tip, E: electrode, F: thermostat, S: high-voltage source, T: telescope with micrometer, cocks: 1—6.

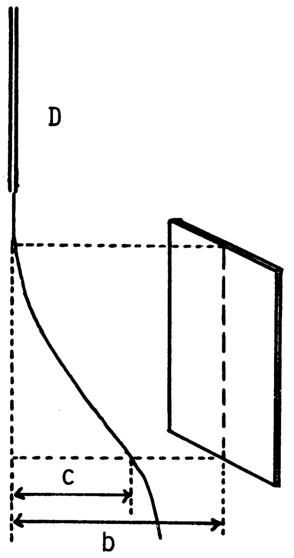


Fig. 2. Arrangement of capillary tip and electrode.

liquid stream was easily varied. The overflow branch B was deviced to make the pressure of the liquid at the capillary tip unchanged and reproducible in order to allow the liquid to flow down steadily during the cource of the observation. The telescope was used to measure the distance between the stream and the electrode to see how far the liquid stream was forced to displace horizontally towards the electrode.

Procedure. After an appropriate portion of the sample liquid in the reservoir C is pumped up to the reservoir A by use of an aspirator, slightly compressed air is applied on the liquid in A through the cock 1 to let the liquid flow down towards the overflow branch B *via* the cock 4. The main flow goes as far as to the capillary tip D through the thermostat F and the cocks 5 and 6 on the way as a steady current, while the overflowed liquid returns directly to the reservoir bottle C. The liquid in C can be used repeatedly. The regulation of the current was carried out at the cock 6. Cock 5 was used only for the interuption of the liquid current. The temperature of the liquid was 25 °C, except otherwise noted. The voltage on the electrode was variable 0—2.5 kV by the DC power supply and was generally kept at 2.5 kV.

In Fig. 2, the arrangement of the capillary tip and the electrode is shown. The distance b denotes the initial separation between the liquid and the electrode with no electric charge, while c is the distance of displacement caused by attraction when the electrode is charged. The distances b and c are measured horizontally at the bottom height of the electrode. Many conples of b and c were determined for the respective sample liquds.

Since the viscosities and the densities of the liquids differ from one another, it is necessary to regulate the flow velocity fixed for the purpose of comparison; the flow velocity was adjusted according to the amount of the liquid fallen during a definite time. The densities of the respective liquids were measured by use of a small pycnometer.

Materials. Water was purified by double distillation after being deionized through ion-exchange resin. Organic substances used were methanol, ethanol, 1-propanol, acetone, acetonitrile, nitromethane, 1,4-dioxane, tetrahydrofuran, acetic acid, dimethyl sulfoxide (DMSO), benzene, nitrobenzene, phenol, and pyridine, and electrolytes used were LiCl, NaCl, KCl, RbCl, $MgCl_2$, $(CH_3)_3NHCl$, and $(C_2H_5)_3NHCl$, all of which were of the special reagent grade, being further purified by distillation or recrystallization for the use.

Results and Discussion

Evaluation of Magnitude of Attractive Force. The distances b and c have been defined above in Fig. 2. In general, the smaller the value of b, the larger becomes that of c; finally the liquid stream may touch the bottom edge of the electrode, where a length A is defined at the extreme distance, as $A \equiv b = c$. Figure 3 shows the relationships of c with b in the case of pure water, in which $\log(b/c)$ is found to be linear with respect to $\log b$ with an empirical formula,

$$\log\frac{b}{c} = m + n\log b.$$

Accordingly, the value of A is obtained by the linear extrapolation of $\log(b/c)$ to zero as equal to $A = 10^{-(m/n)}$. Thus, A is characteristic of the dipolar property of the liquid so far as the temperature and flow velocity are given in a definite electric field.

Since A is an integrated distance of horizontal displacement of liquid attracted towards the electrode with the lapse of time during which the falling liquid stream passes just the vertical length of the electrode. Therefore, the value of A multiplied by the liquid density d may be proportional to the attractive force f wrought on the dipolar liquid ($f \propto Ad$). If it is hypothesized for the sake of simplicity that the electricity on the electrode is a point charge (q) and that the dipolar liquid is fixed at the distance of $b-c$ apart from the point charge, the dipoles of the liquid are attracted by a force f as expressed below:

$$f = -\frac{2\mu q}{\varepsilon(b-c)^3},$$

where μ and ε are the dipole moment and the permittivity of the liquid, respectively. This correlation may hold approximately under the more complicated circum-

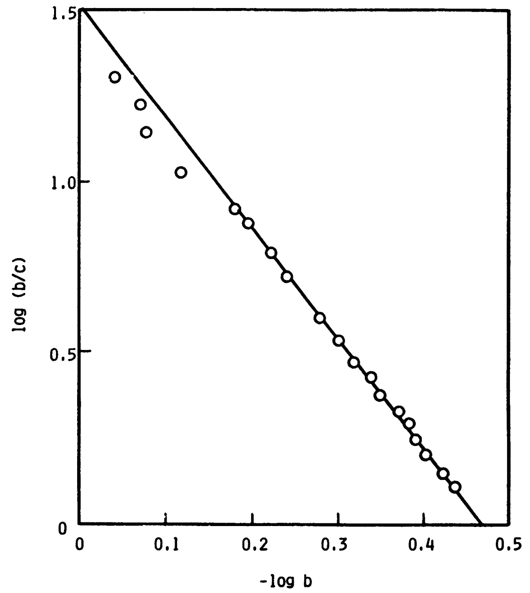


Fig. 3. Linear relationship of $\log(b/c)$ *vs.* $\log b$ in the case of pure water.

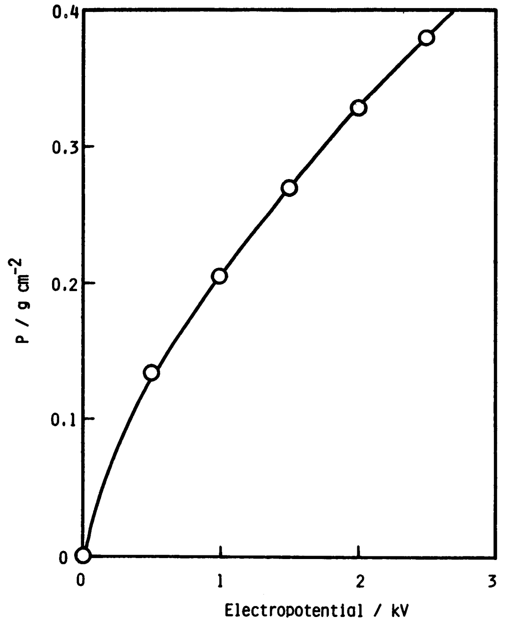


Fig. 4. Correlation of P with the electric potential of the electrode in the case of pure water at a flowing rate 0.810 cm^3 s^{-1} and 25 °C.

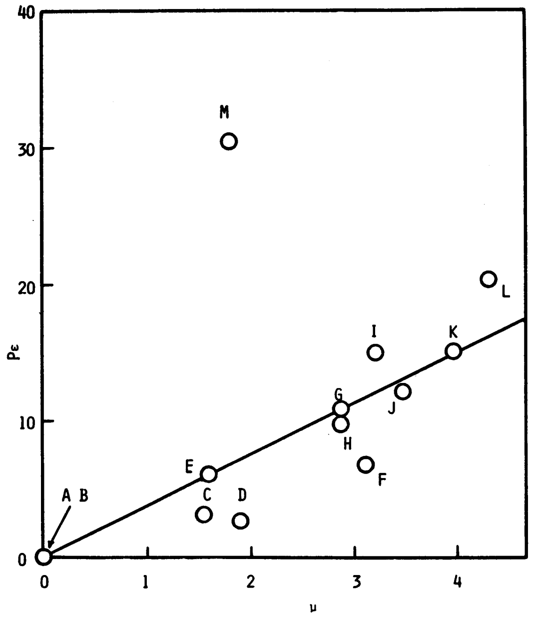


Fig. 5. Proportionality between $P\varepsilon$ and μ.
A: Benzene, B: 1,4-dioxane, C: tetrahydrofuran, D: acetic acid, E: 1-propanol, F: acetone, G: methanol, H: ethanol, I: nitromethane, J: acetonitrile, K: nitrobenzene, L: dimethyl sulfoxide, M: water.

stances like the present experimental conditions, as $f \propto \mu/\varepsilon$. Combining the former proportionality with this, the following equation can be derived, if Ad is denoted by P and k is put as a proportional constant.

$$\begin{aligned} P &\equiv Ad \\ &= k\frac{\mu}{\varepsilon} \qquad (1) \end{aligned}$$

After all, the proportionality of $P\varepsilon$ to μ will be confirmed by measuring A and d for various polar substances, and the obedience to and violation against the proportionality rule may lead us to the discussion on the problems on their molecular structures in liquidous state, as in the followings.

Dependence of P upon Electric Potential of Electrode. Figure 4 shows the correlation of P with the electric potentials of the electrode in the case of water at the flow velocity 0.810 cm^3 s^{-1} and 25 °C. The value of P increases with the increasing potential. In the following observations, the potential will be always fixed at 2.5 kV.

Dependence of P upon Temperature. P exhibited no significant variation with temperature within the range of 10—40 °C, $P=0.39\pm0.03$ g cm^{-2} in the case of water. Nevertheless, the orientation of dipoles in an electric field may be more perturbed by thermal agitation, and therefore P is expected to be smaller at higher temperatures. In the following observations, the temperature will be fixed at 25 °C.

Dependence of A upon Flow Velocity of Liquids. The flow velocity of a liquid current falling down from the tip of the capillary is expressed by $\pi r^2 u$ in cm^3 s^{-1}, where r and u represent the internal radius of the capillary and the current velocity of liquid stream, respectively. On the other hand, since the current velocity u is approximately equal to l/t where l and t are vertical length of the front of the electrode and the time of passing as far as l for the liquid, respectively, the flow velocity is given by $\pi r^2 l/t$. Since A is affected by t, t as well as both r and l should be fixed constant by adjusting the current by use of cock 6, for the purpose of relative comparisons of A with one another among various polar liquids. The flow velocity used throughout the investigation was 0.735 cm^3 s^{-1}. In the cases of different velocities from this value, A was corrected to the standard velocity by virtue of a calibration curve.

Proportional Correlation of Pε vs. μ for Pure Liquids. Figure 5 represents the proportionality between $P\varepsilon$ and μ for 13 pure substances:[4–6] water ($\varepsilon=78.5$, $\mu=1.80$), methanol (32.63, 2.87), ethanol (24.30, 2.89), 1-propanol (20.1, 1.66), acetic acid (6.15, 1.92), acetone (20.7, 3.11), acetonitrile (37.5, 3.45), tetrahydrofuran (7.39, 1.63), 1,4-dioxane (2.21, 0), nitromethane (35.87, 3.23), dimethyl sulfoxide (48.9, 4.30), benzene (2.274, 0), and nitrobenzene (34.82, 3.97). The proportional relationship due to Eq. 1 is well recognized to be approximately established with only one exception of water. When ε, instead of $P\varepsilon$, is plotted against μ for many polar substances, no proportionality is seen but ε grows up more rapidly as μ increases.[7] The reason why only water deviates severely from the proportionality of Eq. 1 is supposed because the used value of dipole moment 1.85 D. U. for water is that in gas phase and the essential value in liquid phase is probably as high as 7, estimated from the proportionality rule, due to the molecular association between themselves forming so-called clusters or icebergs.

Aqueous Mixtures of Some Organic Liquids. The variations of P with the mole fraction x of organic liquids in water are plotted in Fig. 6, where no linearity holds between P and x. But when $P\bar{\varepsilon}$'s are plotted against the

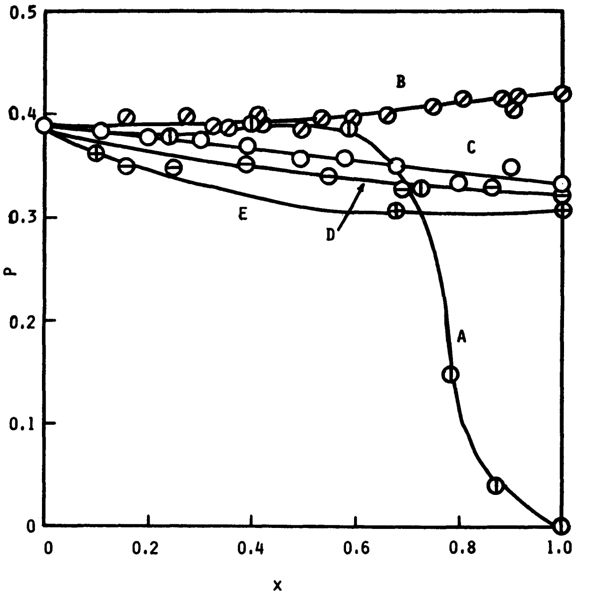


Fig. 6. Variations of P with mole fraction x of organic liquids in aqueous mixtures.
A: 1,4-Dioxane, B: dimethyl sulfoxide, C: methanol, D: acetone, E: 1-propanol.

individual apparent dipole moments of the mixed liquids, $\bar{\mu}$, as shown in Fig. 7, there appear straight lines connecting two limiting points for individual pure liquids respectively. The apparent permittivity $\bar{\varepsilon}$ and dipole moment $\bar{\mu}$ of mixture of two substances 1 and 2 are represented by

$$\bar{\varepsilon} = x_1\varepsilon_1 + x_2\varepsilon_2, \tag{2}$$

$$\bar{\mu} = x_1\mu_1 + x_2\mu_2, \tag{3}$$

at mole fraction x, respectively. The linearities appearing in Fig. 7 indicate that the mixtures behave like pure substances with $\bar{\varepsilon}$ and $\bar{\mu}$ exhibiting their dielectric and dipolar properties proportional to the concentrations of components, although the more delicate and fine properties have been noticed as stoichiometric and structured association of molecules at characteristic mole ratios in the mixtures of water with dimethyl sulfoxide,[8–10] 1,4-dioxane,[10,11] 1-propanol,[12,13] and tetrahydrofuran,[14,15] for instances.

As noticed above, Eq. 1 is valid to normal mixtures as well as pure substances, only if it is modified to be $P = k\bar{\mu}/\bar{\varepsilon}$. Therefore, the variation of P with x_1 may be expressed by the following equation:

$$\frac{dP}{dx_1} = k\frac{\mu_1\varepsilon_2-\mu_2\varepsilon_1}{(\varepsilon_1x_1+\varepsilon_2x_2)^2}. \tag{4}$$

Consequently, the increasing trend at $x_1 \to 0$ can be presumed by

$$\left(\frac{dP}{dx_1}\right)_{x_1\to 0} = k\frac{\mu_1\varepsilon_2-\mu_2\varepsilon_1}{\varepsilon_2^{\,2}}, \tag{5}$$

where the suffixes 1 and 2 correspond to an organic substance and water, respectively. Then, the calculated values of $(dP/dx_1)_{x_1\to 0}$ are in a sequence: dimethyl sulfoxide>acetone>methanol>1, 4-dioxane, which coincides qualitatively with the observed one except for acetone: dimethyl sulfoxide>methanol>1,4-dioxane> acetone, this discrepancy being not interpreted at the present stage.

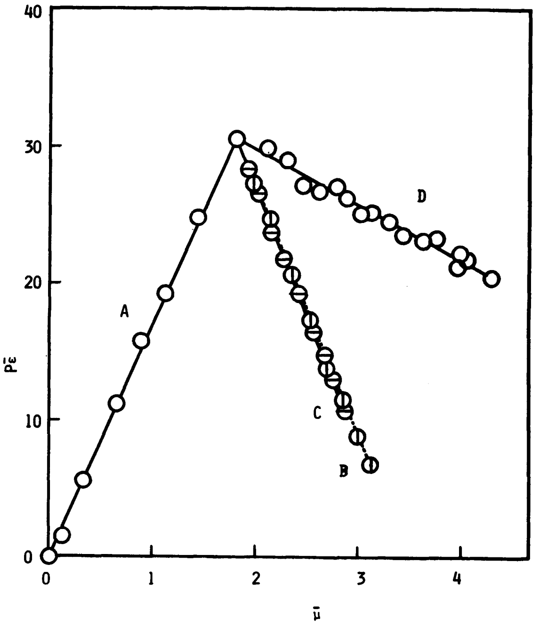


Fig. 7. Linear relationships between $P\bar{\varepsilon}$ and $\bar{\mu}$ for aqueous mixtures of organic substances.
A: 1,4-Dioxane, B: acetone, C: methanol, D: dimethyl sulfoxide.

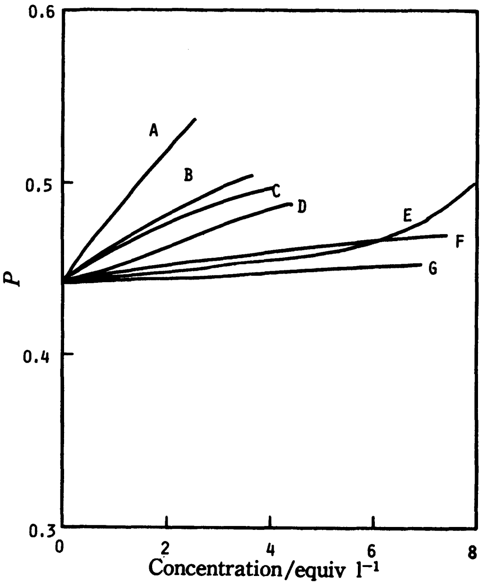


Fig. 8. Variations of P with concentrations of electrolytes in water.
A: RbCl, B: KCl, C: NaCl, D: $MgCl_2$, E: LiCl, F: $(C_2H_5)_3NHCl$, G: $(CH_3)_3NHCl$.
Observations were performed so many times that only smoothed curves are shown as general tendencies in order to avoid the complexity, in the figure.

Aqueous Solutions of Electrolytes. Figure 8 presents the variations of P with respect to the concentrations c/equiv dm^{-3} of electrolytes. The values of $(dP/dc)_{c\to 0}$ are all positive in a sequence: RbCl>KCl>NaCl> $MgCl_2$>LiCl>$(C_2H_5)_3NHCl \approx (CH_3)_3NHCl$. Concern-

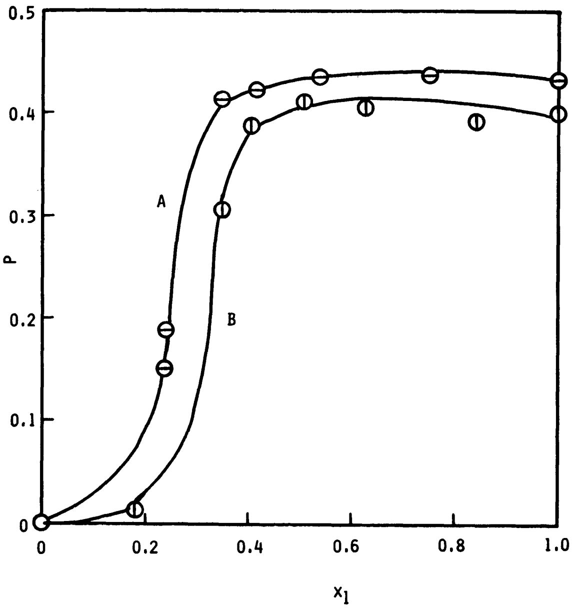


Fig. 9. Variations of P with mole fractions of polar substances in benzene.
A: Nitrobenzene, B: ethanol.

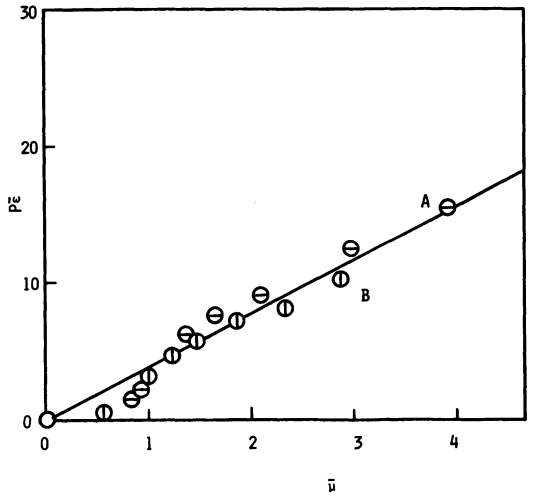


Fig. 10. Proportionality between $P\bar{\varepsilon}$ and $\bar{\mu}$ for benzene solutions of polar substances at various mole fractions.
A: Nitrobenzene, B: ethanol.

ing the cases of alkali chlorides, the observed order coincides with the nature of alkali ions changing from structure breakers to structure formers. Water molecules surrounding ions are classified into three categories, A, B, and C; water molecules in A layer are firmly attached to the central ions by the Coulombic interactions between ion and dipole, and water molecules in C range are bulk water having the ordinary nature as pure water, while water molecules in B layer are located intermediate between A and C and therefore are free from the restrictions due to both the Coulombic attraction as in A and the hydrogen bondings between themselves as in C. Accordingly, the electric dipoles of water molecules in B layer may be enabled to take proper orientations towards the outer electric field more easily than those in A or C area.[16] The structure-breaking ions have more water molecules in B layer and therefore aqueous solutions of structure breakers may exhibit larger P value than the structure making ions. The observed order of the values of $(\mathrm{d}P/\mathrm{d}c)_{c\to 0}$ is thus well understood.

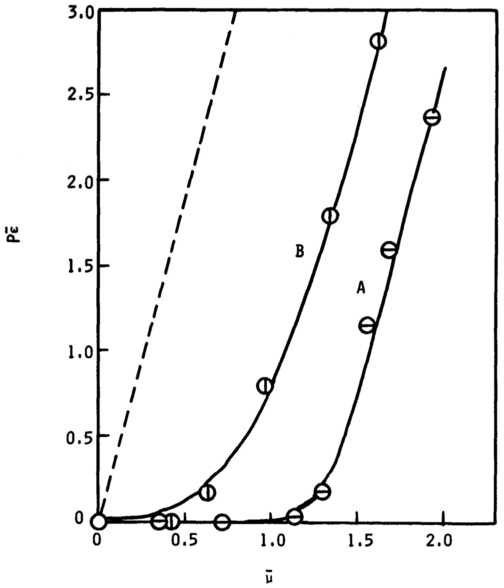
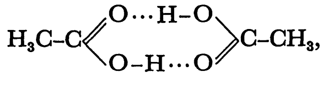


Fig. 11. Variations of $P\bar{\varepsilon}$ with $\bar{\mu}$ for benzene solutions.
A: Acetic acid, B: tetrahydrofuran.

Although $(C_2H_5)_3NH^+$ and $(CH_3)_3NH^+$ ions have large ionic radii, they are not structure breakers but structure makers, because the hydrophobicity of CH_3 and C_2H_5 groups promotes the icelike hydrogen-bonded structure around ions.[17] This is the reason why alkyl ammonium ions exhibit smaller value of $(\mathrm{d}P/\mathrm{d}c)_{c\to 0}$ than Li^+ ion.

Benzene Solutions with Polar Substances. In order to make the matter simpler, we used mixtures of polar substances with nonpolar liquid: benzene with $\mu_2=0$ and $\varepsilon_2=2.274$. In this case, Eq. 5 becomes $(\mathrm{d}P/\mathrm{d}x_1)_{x_1\to 0}=k\mu_1/\varepsilon_2$. Although Fig. 9 shows that the correlationship between P and x_1 do not explicitly exhibit the expected slopes at the limiting concentration $x_1\to 0$ in mixtures of nitrobenzene or ethanol in benzene, respectively, the proportionality of $P\bar{\varepsilon}$ *vs.* $\bar{\mu}$ is approximately established over the whole concentration range for both mixtures, as shown in Fig. 10. This fact may indicate that individual molecules of both nitrobenzene and ethanol exist independently and freely in benzene without occurrence of any molecular association, respectively.

On the other hand, Fig. 11 shows the cases of benzene solutions of acetic acid and tetrahydrofuran, in which no proportionality is recognized between $P\bar{\varepsilon}$ and $\bar{\mu}$. Therefore, it seems that they are not simple mixtures but there probably happen mutual interactions between polar molecules of themselves in benzene solutions. Acetic acid is known to dimerize by hydrogen bondings in benzene, giving


$$H_3C\text{-}C\begin{matrix}\nearrow O\cdots H\text{-}O\searrow \\ \searrow O\text{-}H\cdots O\nearrow\end{matrix}C\text{-}CH_3,$$

which has a nonpolar structure and therefore may dimi-

Table 1. Examination for additivity of $P\bar{\varepsilon}$ between phenol and pyridine in benzene solutions

Solute	x	$\bar{\varepsilon}$	$\bar{\mu}$	$P\bar{\varepsilon}$
Phenol	0.4	5.276	0.588	0.280
Pyridine	0.4	6.284	0.972	0.798
Mixture of phenol and pyridine	0.4 0.4	9.287	1.560	3.752

nish the apparent dipole moment, making the solutions to disobey the proportionality correlation in the result. Tetrahydrofuran also fails to obey the proportionality rule to the similar direction to acetic acid. But the reason for the depression of its apparent dipole moment in benzene is not understood at the present stage of the investigation.

As has been indicated in Fig. 5, the observed point for water appears far above the straight line of the proportionality between $P\varepsilon$ and μ. The apparent increment of μ is supposed to be caused by the molecular association of the type head to tail $(+-)(+-)\cdots$, while the apparent depression of μ as experienced in the case of acetic acid and presumably that of tetrahydrofuran in benzene solutions may be attributed to the formation of dimers of the type head to head $(+-)(-+)$.

Ternary Mixtures of Phenol, Pyridine, and Benzene. If two solutes S_1 and S_2 are independently dissolved in benzene without mutual interaction between molecules of the same species as well as between the different ones, an additivity correlation with respect to $P\bar{\varepsilon}$ values should hold in solutions of the both solutes. Table 1 gives data proving whether the additivity holds in the cases of phenol ($\varepsilon=9.78$, $\mu=1.47$) and pyridine (12.3, 2.43) or not. According to the table, the observed $P\bar{\varepsilon}$ for the ternary mixture of phenol ($x=0.4$), pyridine ($x=0.4$), and benzene ($x=0.2$) is 3.752, which is much larger than the value of the sum of the respective solutions in benzene of the same mole fraction, $0.280+0.798=1.078$. This discrepancy may suggest that there occurs molecular association between phenol and pyridine, forming a molecular complex with apparently large dipole moment as compared with those for respective species. Although the detailed structure of the molecular complex is not clear, the bonding between the two species would be a hydrogen bond of the type O-H···N and the resultant electron density at benzene ring may be larger than that at pyridine ring. Thus, the point for the observed $P\bar{\varepsilon}$ should appear above the simply expected one from the additivity as a normal mixture, in a $P\bar{\varepsilon}$-$\bar{\mu}$ diagram.

Conclusion. The attractive force wrought on polar substances in an outer electric field has been found to be proportional to the observable quantity P as defined above. The value of P offers a simple means to detect the structures of pure liquids or mixtures in liquids. $P\varepsilon$ *vs.* μ for various pure liquids and $P\bar{\varepsilon}$ *vs.* $\bar{\mu}$ for mixtures of some components give a straight line with a common proportional constant k, if no molecular association occurs, although ε *vs.* μ for various polar substances is not linear.

When $P\bar{\varepsilon}$ value *vs.* $\bar{\mu}$ fails to come on the straight line with the slope k, there probably happens to take place molecular association. The association to cause an apparently larger dipole moment makes the point locate above the straight line, and *vice versa.* The former instances are seen in the cases of water and mixture of phenol–pyridine–benzene, and the latters in those of mixtures of acetic acid—benzene and of tetrahydrofuran–benzene.

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