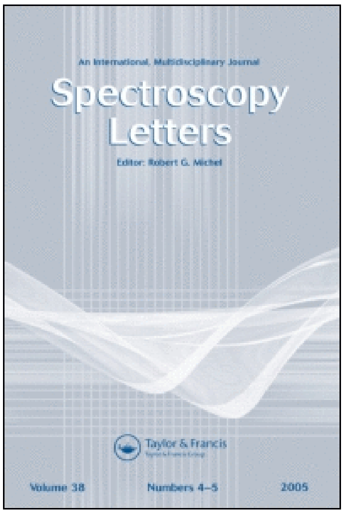

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Spectroscopic Investigation on Critical Concentration of Aqueous Electrolyte Solution

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SPECTROSCOPIC INVESTIGATION
ON
CRITICAL CONCENTRATION
OF
AQUEOUS ELECTROLYTE SOLUTION

KEYWORDS: Solute-solvent Interaction, Aqueous Solution, Critical Concentration, Propylene Carbonate, Alkali Halide, UV, C-13 NMR, IR

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ABSTRACT

It has been assumed that the structure of binary solution may change depending on the molar ratio of solute to solvent and refer to the presence of some critical concentration where solute-solvent interactions change. Spectroscopic investigation on aqueous solutions of propylene carbonate and alkali halides have really shown presence of critical concentrations. Furthermore, the latter critical concentration of aqueous alkali halide solutions has revealed concern with the reactivity of iodide ions which have been added to the solutions. The latter finding will be the first observation of the concern between structure and reactivity of aqueous solutions.

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I INTRODUCTION

Most experimental and theoretical investigations on aqueous solutions have so far been directed to the study on interionic effects and the problem, which has been referred to by Franks[1)]as ions may cause significant change in the properties of solvent, remains not sufficiently elucidated even at present.

Vaslow has reported observation of discontinuity in molal volumes of alkali halide aqueous solutions.[2)] Although the latter report is valuable in showing experimental evidence for discontinuous property of aqueous solutions, however, as it remains qualitative in nature, further investigation on aqueous solutions by molecular spectroscopy seems necessary and useful.

Present authors will report the results of recent investigations which refer to discontinuous change of spectroscopic properties of aqueous solutions of propylene carbonate, PC, 4-methyl-1, 3-dioxolan-2-one, and of alkali halides. The basic idea of present investigation is to see the concern of composition of solution, R, the molar ratio of solute to solvent, with solute-solvent interactions. The latter interactions in sample solutions are investigated by NMR, UV, IR and by the reactivity of iodide ions which are added to alkali halide aqueous solutions. It is assumed here that if R is small, some of the solvent molecules are left free, being not bound to the solute, whereas, when R getts large, the number of free solvent molecules is reduced and finally becomes zero at some critical concentration. In the latter situation, all solvent molecules may be taken as associated with solutes either by direct or indirect solvation. At or beyond the latter condition of R, the solute-solvent interactions are assumed to occur among solvated solutes or between solvent and solvated solutes. Thus, critical concentration, C_{cr}, can be defined as the concentration which refers to the critical R cited above. Concrete values of C_{cr}'s will be reported for various systems.

II EXPERIMENTAL

A PC-H_2O SYSTEM

Reagent:

Propylene carbonate, PC, which was purchased from Wako Pure Chemical Reagent Co., was allowed to stand for 24 hrs in contact with molecular sieve of Kanto Chemicals Co. Inc., Cicasorv Z type 420, and then distilled twice under nitrogen atmosphere of about 20 mmHg. Only the middle of distillate was used for the experiment. Water content of the latter sample of PC was determined as about 100 ppm. For the convenience of further discussion, the latter PC will be referred to hereafter as purified PC. The PC samples of different amounts of water were prepared by adding water to purified PC. Water contents of all samples were determined by Karl Fisher titration.

Apparatus:

Water content of PC was determined by Aquatest SS-202 of Shibayama Scientific Co. Ltd. made. The C-13 NMR was measured by JEOL JNM-FX-270 in pulsed Fourier transform mode at the JEOL Research Laboratory, Akishima. The UV spectra were measured with Shimazu double beam spectrometer UV-200 with Shimazu Recorder U-125 MU at Chiba University. The IR measurements were made by Digilab ETS-20 C/D Fourier transform infrared spectrometer at the Central Research Laboratory of Kuraray Company.

Results:

The UV absorption spectra are reproduced in Fig. 1, where the isosbestic point is observed. The latter refers to the fact the PC-H_2O system is formed of two

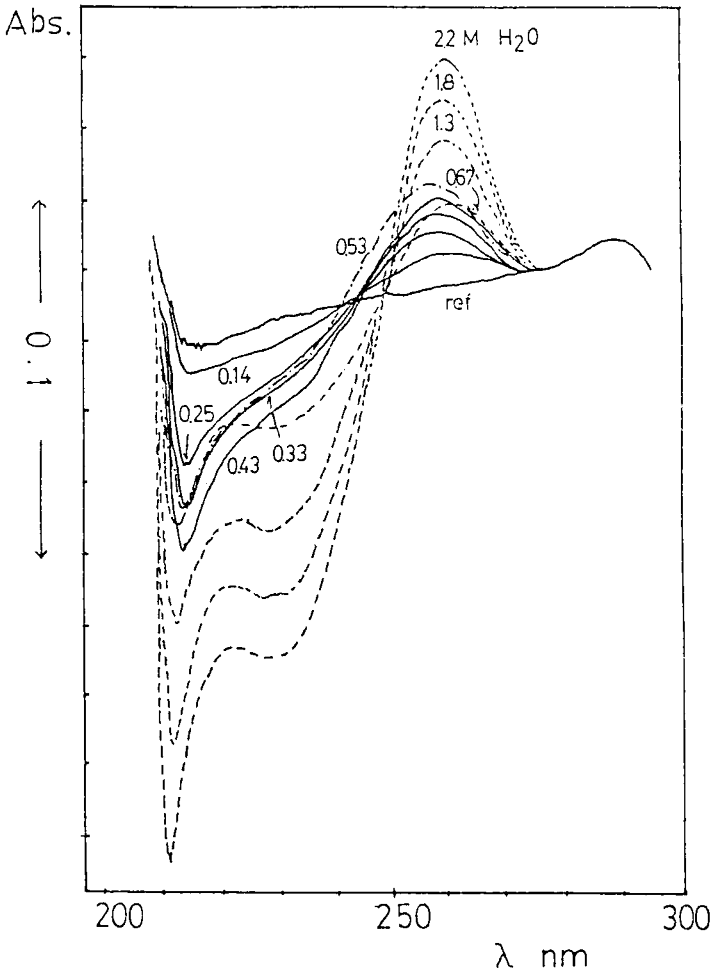

Fig. 1. UV Spectra of the Binary Solutions of Propylene Carbonate and Water.

TABLE 1

C-13 NMR Chemical Shift (ppm) for Propylene Carbonate

H_2O(M)	C=O	CH	CH_2	CH_3
0.01	136.861	55.583	52.316	0.000
0.067	136.861	55.583	52.316	0.000
0.33	136.909	55.631	52.365	0.048
0.67	136.958	55.680	52.365	0.048

phases, X and Y, which are in equillibrium with each other. Phase X refers to the composition of H_2O less than 0.5M per 1M PC and Y with H_2O more than 0.5M.

Table 1 shows the results of C-13 NMR measurements. The methyl carbon of purified PC was taken as the reference for the chemical shift of C-13 NMR. As seen in Table 1, no chemical shift is observed with respect to all species of C-13 between reference and the sample of 0.01 or 0.067M H_2O. Accordingly, the results of C-13 NMR suggest that the electronic surroundings of all functions of PC are apparently not changed by H_2O up to about 0.1M so as to produce C-13 NMR chemical shift. With H_2O more than 0.33M, C-13 signals of all functions begin shift. However, the magnitude of the shift is same with respect to all functions of C=O, CH, CH_2 and CH_3. It is to be noted that the samples with H_2O below 0.33M belong to X. The carbon atoms in the sample of 0.67M H_2O, which belong to the Y phase, show chemical shifts which are different from each other. Namely, carbon atoms of C=O and CH show same shift being lower than those of CH_2 and CH_3. The difference between the latter two is 0.05 ppm. It should be noticed here that the latter value is equal to the shift value for all carbons of PC with 0.3M H_2O. Hence, the results cited above will suggest that PC with H_2O below about 0.3M behaves as a nonelastic ball in water, cf. Fig. 2a. Elastic interaction starts in the samples with H_2O more than about 0.3M. However, the interaction in the latter samples is assumed not specific with respect to the functions of PC, cf. Fig. 2b. In the sample of 0.6M H_2O, the interactions between PC and H_2O get specific with respect to the functions. Namely, CH_2 and CH_3 remain not changed showing same chemical shift as that of ca. 0.3M H_2O PC, whereas, CO and CH are shifted to the lower field. The latter finding refers to the fact that a kind of chemical bond has been formed between PC and H_2O at CO and CH, cf. Fig. 2c. Thus, the results of C-13 NMR measurements suggest that C_{cr} for PC and H_2O lies in a range between 0.3 and 0.6M around of water. With the consideration of the results of UV measurements, 0.5M will be referred to as the value of C_{cr} for PC-H_2O system.

The aforementioned results may be interpreted following. The PC molecules in the purified sample are assumed to be associated with each other as the result of high dielectric constant of the molecule. As H_2O molecules are introduced into PC, association among PC molecules are destructed and interaction between PC and H_2O starts. The latter interaction is first isotropic in so far as R is samll, not specific with respect to the functional groups of PC. Specific bonding between PC and H_2O is formed when H_2O getts more than 0.5M, forming a kind of compound of PC and H_2O. In the samples with H_2O more than 0.5M, the latter compound is assumed to behave as new solute in PC. The scheme cited above does not deny the possibility of the exchange of water molecules among PC molecules. Figure 2 presents a shematic diagram of the interactions between PC and H_2O, where (a) refers to the nonelastic mixture of PC and H_2O, (b) a solution of H_2O in PC where a weak and isotropic interactions work and (c) a system where

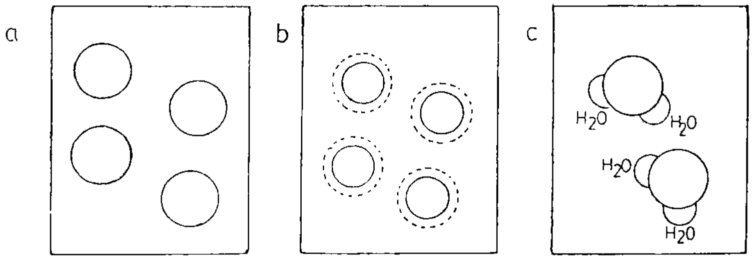

Fig. 2. Shematic Model of PC-H_2O after C-13 NMR Measurements.
Round Circle refers to PC Molecule.
a) PC and $H_2O<0.1M$, where PC-H_2O Interaction is nonelestic.
b) PC and $H_2O = 0.1-0.5M$, where PC-H_2O Interaction is elastic, but isotropic.
c) PC and $H_2O>0.5M$, where PC-H_2O Interaction forms Compound.

compounds of PC with H_2O are formed and embedded in the media of PC.

It is possible to assume that about twenty molecules of PC interact with one H_2O molecule when scheme (b) starts, because isotropic shift of PC starts at around 0.05M H_2O, while in (c), two, because the range of (c) starts at 0.5M H_2O. Thus, equations (1) and (2) may hold for (b) and (c), respectively.

$$H_2O + 20PC = M_x \qquad (1) \text{ and}$$
$$H_2O + 2PC = M_y \qquad (2),$$

where, M_x and M_y denote the chemical species of compounds of PC and H_2O in the X phase and Y phase, respectively. With the data of Tab. 1, equillibrium constants for (1) and (2) have been calculated as $2X10^{-23}$ and $10^{-3 \text{ or } -2}$, respectively.

B Aqueous Alkali Halide Solutions

Alkali halides:

Extra pure grade salts were purchased from Wako

Pure Chemical Reagents Co. Ltd. and used without any further purification.

Water:

Same water as described in the experiment A was also used in the present experiment. Sample solutions were put to experiment one day or at least several hours after preparation.

Spectrometers:

Same as those in the experiment of A.

Results:

The features of the IR spectra are same to each other among all kinds of alkali halide solutions examined. Typical example of the spectra is shown in Fig. 3 for NaCl solutions. Band at ca. 3500 cm^{-1} may be attributed to OH stretching of monomer H_2O. It will be referred to as the OH band hereafter. The intensity of the latter band has shown a remarkable concentration dependence. It is reduced with the increase of salt concentration until it reaches a value of about 0.5M. Beyond the latter concentration, it levels off. Hence, the results of IR measurements suggest that 0.5M may be the C_{cr} for NaCl solution. All other salts have shown similar features, but different values of C_{cr}'s, as 0.2, 0.4, 0.05 or 0.1, and 0.3 or 0.4M for LiCl, KCl, CsCl, and $(NH_4)_2SO_4$, respectively. Further evidence for the discontinuous properties of the alkali halide solutions is being noticed now in the laboratory of the present authors with respect to the refractive indices of the solutions.[3)]

C Salt Effect on the Redox Reaction of Iodide Ions

It has long been known that the iodide ions in sea water can not directly be determined by solvent extraction. Accordingly, a laborious indirect method has been

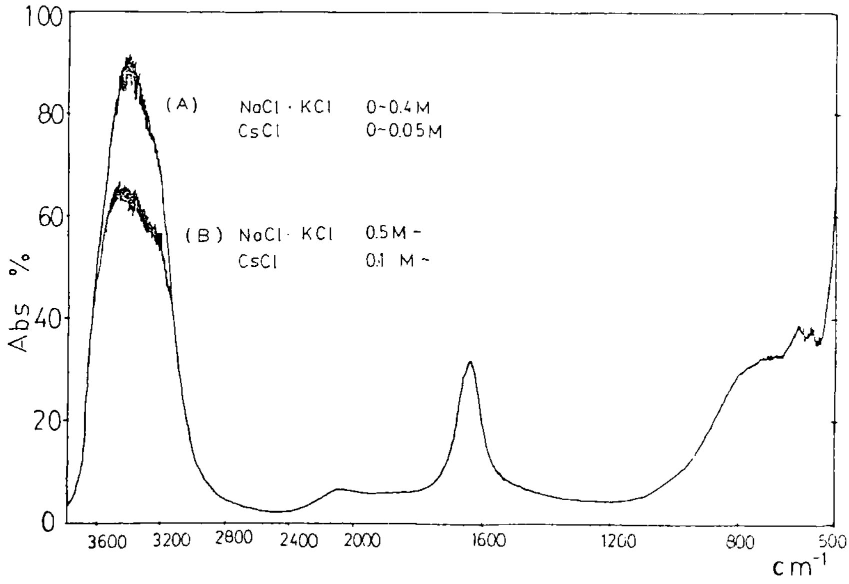

Fig. 3. IR Spectra of Aqueous Solutions of NaCl and Other Salts.

adopted.[4)] Present authors have carried out a detailed investigation on the salt effect for the solvent extraction of I^- ions, and found that the latter effect deeply concerns with the critical concentrations cited above. The I^- ions in aqueous acidic media can be oxidized by nitrous acid according to quation (3), and extracted by carbon tetrachloride.

$$2I^- + NO_2^- + 2H^+ = I_2 + NO + H_2O \qquad (3)$$

However, the reaction (3) is heavily disturbed by the copresence of NaCl. Fig. 4 shows the salt effect on extractability of I^- ions. Actual procedure of experiment is following. Iodide ions in 30 ml of 10^{-5} M KI solutions with different amounts of NaCl were extracted by 10 ml CCl_4 after the reaction of (3). As seen in the figure, extraction is performed with almost 100%

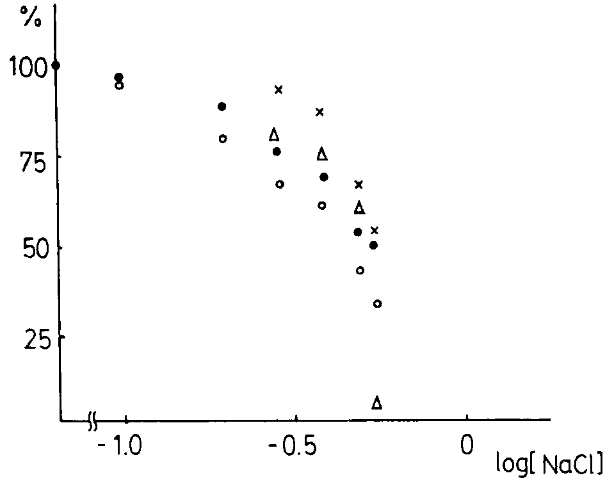

Fig. 4. Extractability of I^- as the Function of NaCl Concentration. The Absissa refers to the Logarithmic Concentration of NaCl and the Ordinate Relative Extractability as measured by the Absorbance of I^- extracted in CCl_4. Each of different Symbols refers to the different Run of Experiment.

recovery for the solutions with NaCl below 0.3M. Recovery drops markedly with NaCl over 0.4M, and becomes almost zero at 0.6M. Similar effect of salt has been observed with LiCl and KCl too. It is very remarkable that the concentrations of salts which show disturbance are 0.2 and 0.4M for LiCl and KCl, respectively, and consistent with the concentrations which have shown characteristic change of OH band intensities.

In accordance with the findings cited above, present authors have noticed that reaction (3) can proceed in paralell with the appearance of a specific band of UV spectrum at 250 mμ. Figure 5 presents the UV spectra for simple aqueous NaCl solutions of various salt concentrations. The absorption bands in the figure

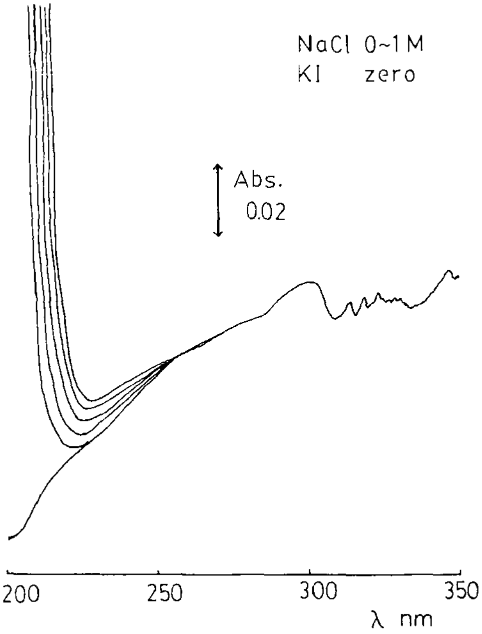

Fig. 5. UV Spectra of Aqueous Solutions of NaCl with no I^-.

may be assigned from the lower frequency side to higher one as the charge transfer (CT) band at 200 mμ, and the n-π excitation band at 225 mμ. All solutions of other alkali halides, LiCl, KCl, RbCl and CsCl, show similar spectra. As I^- ions are added to the solutions, it is noticed that a new band appears at 250 mμ as shown in Fig. 6. Molar absorption coefficient for the latter band is determined as 1.0 for NaCl solutions. It has been noticed that the intensity of the 250 mμ band is heavily dependent on the concentration of salt. (cf. Fig. 7) It is increased with salt until the latter reaches the characteristic concentration at which the I^- extraction is disturbed. Beyond the latter concentration, the intensity of the 250 mμ band is reduced.

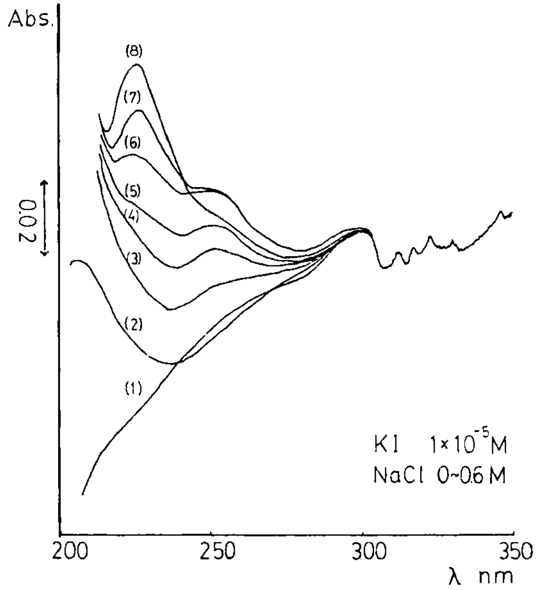

Fig. 6. UV Spectra for Various Solutions of NaCl with 10^{-5}M KI. Numbers in the Figure from (2) to (8) refer to the Concentrations of NaCl, 0, 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6, respectively, and (1), Baseline. Intensity of 250 mμ Band is highest for (7) and getts lower for (8).

Thus, the 250 mμ band is a keyband for the redox reaction of I^- ions.

III DISCUSSION

As a matter of fact, all results of spectroscopic investigations shown above seem consistently to refer to the presence of C_{cr}'s in aqueous solutions, and to suggest discontinuous structure of the solution. The latter may refer, furthermore, to the discontinuous change of the electronic properties of the solution.

The 250 mμ band, which has been noticed as the key band for the redox reaction of I^- ions, sites beside

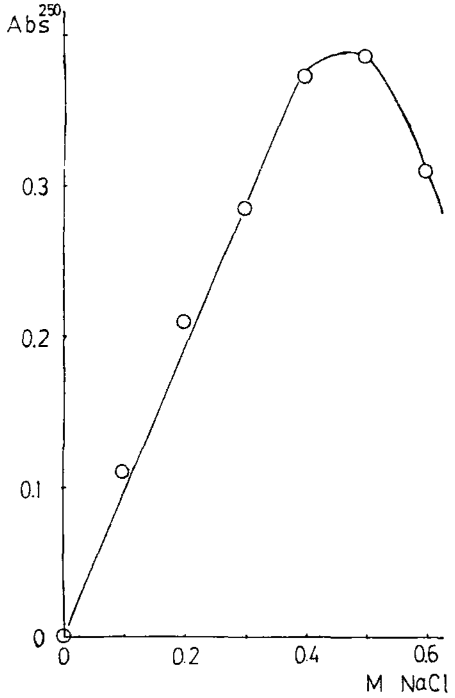

Fig. 7. Absorbance of 250 mμ Band as the Function of NaCl Concentration

the CT band at 200 and the n-π band at 225 mμ. This fact may suggest that the solutions which present 250 mμ band carry electrons which are more labile than CT or n-π excitations. Namely, very labile electrons are formed in specific structure of solutions.

At this stage of the discussion, it will be worthwhile to refer to the reports of 250 mμ in the literature. All reports in the literature seem to show concern with labile electrons. Atomic absorption has been observed at 250 mμ with mercury in the condensed phase.[4)] The latter certainly refers to the excitation of 6s electron. Another case of observation of 250 mμ

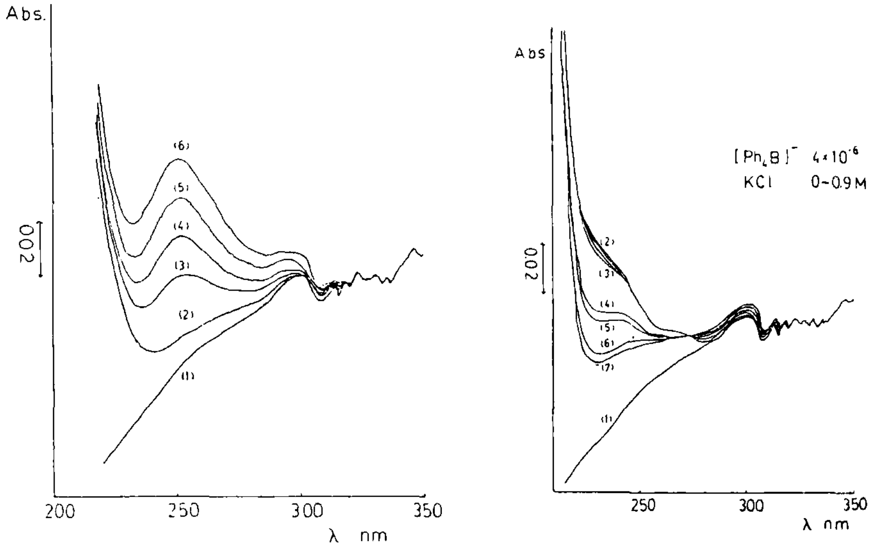

Fig. 8. Observation of 250 mμ UV Band in the Aqueous Solutions of Cu^{2+} and Ph_4B^- ions.
a) KCl and $CuCl_2$(10^{-4}M). Numbers in the Figure refer to the Concentrations of KCl, from (2) to (7), 0, 0,1, 0.2, 0.3, 0.4, 0.5 and 0.6, respectively, and (1), Baseline.
b) KCl and Ph_4B^-(4×10^{-6}M). Numbers in the Figure refer to the Concentrations of KCl as (2) to (7) to 0.4, 0.5, 0.6, 0.7, 0.8 and 0.9M, respectively and (1) to Baseline.

band has been reported with respect to thallium embedded in solid NaCl.[5] The latter apparantly the assistance of NaCl matrix for the electronic excitation of thallium. In addition, the present authors have examined salt effect on other systems which apparently seem to hold labile electrons. The UV absorption bands have been measured for the aqueous solutions of alkali halides to which cupric ions or tetraphenyl boron ions, Ph_4B^-, have been added. Fig. 8a presents the spectra of aqueous KCl solutions added with $CuCl_2$ and Fig. 8b those with Ph_4B^- ions. The 250 mμ band is observed also in both cases. As it has been mentioned already, simple aqueous solution of KCl does not show the latter band.

Thus, the solute-solvent interactions are strongly affected by the solute ions so as to be classified as different from each other depending on the condition of the solution either below or beyond the critical concentration. It should be noticed, furthermore, that the latter difference refers to the concern of solution with its reactivity. The latter finding will be the first observation of the fact that structural change of solute-solvent interactions relates with the reactivity of solution.

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