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Phase Diagram and Electric Conductivity in the Binary System:

Picric Acid—*o*-Bromoaniline

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Phase diagram of a binary system with a complex isomers pair, picric acid (PiOH)–o-bromoaniline (BrA) has been elaborated by scanning calorimetry. Two compounds have been found in the system viz. BrA·PiOH (melting point 408 K) and $(BrA)_2 \cdot PiOH$ (incongruently melting at 342 K). BrA·PiOH forms solid solutions with both PiOH and BrA in the concentration range extending from 45 to 52 mpc PiOH. Temperature of the phase transition salt/complex amounts to 375 K for stoichiometric Bra·PiOH and 370 or 377 K for terminal solutions with excess of PiOH or BrA respectively. Heat of transition for stoichiometric compound amounts to 24.7 kJ/mole. Dc-electric resistivity of BrA·PiOH increases in the course of the salt/complex transition.

INTRODUCTION

Some picrates and nitrophenolates of aromatic amines are known[1] to form two solid modifications differing both in crystal structure and in type of chemical bonding.[2] In the low-temperature phase acid-base interactions between picric acid and amine molecules dominate and a salt (ionic pair) structure ($AH^+ \cdot PiO^-$) results. In the high-temperature phase, however, CT-interactions prevail and a weak CT-complex (A·PiOH), similar to the complex of appropriate amine with trinitrobenzene is formed. The name "complex isomers" has been proposed by Hertel[1] for this singular class of compounds in which phase transition is induced by chemical reaction. Although both forms: salt and CT-complex can coexist in any liquid solution[3] no data of the equilibrium constant are available hitherto. In a solid state, however, the phase rule excludes the existence of equilibrium between the isomers besides the transition point and only one of them is stable at any temperature differing from transition temperature. We have proved by specific heat measurements that isomerization is a first order transition, in *o*-bromoaniline picrate at least.

There are distinct differences in physical properties between both complex isomers of any phenolate. We shall discuss them for *o*-bromoaniline picrate as an example. The salt/complex transition manifests itself by replacement of NH_3^+-bands by NH_2-bands in IR spectrum[4] and by change of colour from yellow to dark red, caused by an appearance of CT-band in visible. The density increases by about 10% upon the transition,[5] the effect differs, however, both in sign and in magnitude amongst other complex isomer pairs.[6] Crystal structure of *o*-bromaniline picrate is not elaborated hitherto, but the data available provide a general view on molecular packing in crystals of two other complex isomers: 1-bromo-2-naphthylamine picrate and 2,6-dinitrophenolate of 1-bromo-4-naphthylamine.[6,7] In the crystals of the salt modification the NH_2 and OH groups of adjacent molecules are in close contact being linked by hydrogen bonds; crystals of complex form contain neutral molecules of components, bonded by the CT-interaction between the ring systems of acid (acceptor) and base (donor) molecules. Description presented above exaplains the difference in heat of formation of isomers, e.g. -13.4 kJ/mole for the salt form and less than 0.4 kJ/mole for CT-complex in 1-bromo-4-naphthylamine with 2,6-dinitrophenol system.[3]

Complex isomers are interesting objects to study of the relationship between electric conductivity and type of bonding in organic solids. The change in conductivity upon the salt/complex transition has been recently measured[2,8] for several complex isomer pairs on purpose to compare the conductivity of both isomeric forms, and a sharp decrease in resistivity and its activation energy has been found for 1-bromo-2-naphthylamine picrate and for 1-chloro-2-naphthylamine picrate.

One must be extremely cautious, however, when interpreting such measurements in binary systems. It has been observed in the system anthracene–acridine[9,10] that the presence of even a small amount of liquid phase appearing in course of eutectic melting caused the resistance of the sample to decrease dramatically. Similarly in any binary system e.g. CT-complex, traces of eutectic liquid may appear far below the true melting point of stoichiometric compound as a result of unintentional deviation from ideal stoichiometry, affecting the results of measurements of electric conductivity. Such deviation might arise during the sample preparation, especially if material was crystallized from solution which is the most convenient and commonly used way.

To exclude the spurious results one has to study the phase diagram of the system in details, at least in the neighbourhood of the stoichiometric composition of the complex. Here the approach is presented for *o*-bromoaniline picrate. The phase diagram of this system has been already outlined by Hertel,[1] who derived the approximate position of the liquidus line by the observation of material melted in capillary tubes. This paper comprises a more detailed study of the system by scanning calorimetry and hot-stage microscopy.

EXPERIMENTAL

o-Bromoaniline (BrA) has been synthesized in this laboratory, then purified twice by crystallization from ethanole and eventually by column chromatography on alumina. The snowy product crystallizing in long needles could by stored for a long time in refrigerator without any marks of oxidation. Picric acid (PiOH) (commerical product) was precipitated from ethanole and dried in vacuum for one week at room temperature. Appropriate amounts of components were weighted up in glass tubes, then sealed under pure helium, melted and vigorously stirred. Dark red or yellow liquids were rapidly cooled and ground to powder. Samples were left to equilibrise at least for two weeks prior to any investigation. Calorimetric studies were carried out using Perkin–Elmer DSC-1B scanning calorimeter at standard heating rate 4 deg/min. The samples were encapsulated in aluminium capsules during experiments.

Additional relevant information was provided by direct observations of material sealed in flat glass micro-tubes and heated on hot-stage of a microscope. Phase changes occurring in single microcrystals could be noticed because of a colour change accompanying the transition. The onset of melting was also noticeable under appropriate magnification (150 ×). It was an obligatory precaution to seal the samples in capsules or tubes to obtain correct results in the experiments. Material containing more than 50 mpc of BrA when kept in an open vessel loses BrA by sublimation already at room temperature, and the rate of this process increases rapidly at elevated temperatures.

CALORIMETRIC STUDY

Stoichiometric *o*-bromoaniline picrate shows two endothermic effects during heating: a salt/CT-complex transition at 375 K, and melting at 408 K, the ΔH values being 24.7 and 28.4 kJ/mole respectively. The value of the heat of transition roughly coincides with that reported by Matsunaga[2] (28.1 kJ/mole) who has found it decreasing within 20% upon grinding the sample. The value of transition temperature given here differs from those found by Hertel (368 K) and Matsunaga (376–383 K)[1,2] for materials precipitated from solution. We have found, however, that transition temperature depends on solvent used in crystallization, and the samples crystallized from benzene, ethanole, and chlorobenzene showed the onset of transition at 375, 378 and 380 K respectively. Though there is no direct evidence that the materials contained solvent affecting the transition temperature, samples obtained by melting seems to provide more reliable results.

In samples containing more than 52 mpc PiOH salt/complex transition appeared at constant temperature of 370 K. The peak on DTA-curve overlapped the subsequent peak of eutectic melting at 375 K. It was unfeasible to separate these peaks satisfactorily. We did succeed, however, to observe a single peak of eutectic melting if DTA run was repeated immediately after cooling down the sample melted previously. The high-temperature phase undercools under these conditions and no peak at 370 K appears upon heating. Reverse transition CT-complex/salt was rather slow at room temperature and took several hours to complete.

The samples containing 60–88 mpc of PiOH when heated for the first time revealed another endothermic effect at 367 K. The maximum of this effect was observed in samples containing 70 mpc PiOH. The peak was absent, however, in subsequent runs.

Much more complicated phase equilibria have been revealed for materials with an excess of BrA. Salt/complex transition was observed at 377 K in samples containing up to 76 mpc of BrA. Extremely small effect depending in shape and value on the heating rate and overlapping the melting peak was found even in a sample containing 80 mpc of BrA (Figure 2). As follows from the phase diagram (Figure 1), melting in this material should be completed already at 373 K thus the appearance of the transition peak should be interpreted as an artifact caused by nonequilibrium conditions of the sample studied by DSC-method.

Two other isothermal endothermic processes were observed in materials rich in BrA. That at 342 K culminating for 66 mpc BrA sample is due to incongruent melting of the solid compound $(BrA)_2 \cdot PiOH$. The second, at 302 K, represents melting of a eutectic formed between this compound and free BrA. Only a rough estimation of eutectic composition (less than 2 mpc of PiOH) was possible, the melting temperature of eutectic and *o*-bromoanaline being nearly the same (302 and 304 K respectively).

Another type of effect was noticed for samples containing 52–65 mpc of BrA. It manifests itself on thermograms by a broad diffuse peak appearing in the temperature range of 290–340 K (cf. line **a** in Figure 1) and increasing in intensity with increase in amount of BrA. An additional microscopic observation revealed that at nearly the same temperature in the originally two-phase material red phase transformed slowly into yellow one. Thus the effect was attributed to the coalescence of two phases viz. nonstoichiometric 1 : 1 complex in salt form and 2 : 1 complex, occurring by decomposition of the red 2 : 1 complex and dissolution of excess amine in the yellow salt phase.

Quite different behaviour has been observed for all samples containing more than 50 mpc of BrA when DTA was repeated shortly after completion of the first run. The obviously metastable material did not reveal any effects connected with existence of 2 : 1 complex and showed instead a peritectic peak on DTA curves at 353 K. This nonequilibrium diagram will not be discussed here.

DISCUSSION

The complete phase diagram obtained in this work is shown in Figure 1. All lines in this diagram but this labelled **a** are derived by the analysis of DTA-curves. Thus the position of liquidus line is given only approximately, because of limitations inherent to the DTA method.

o-Bromoaniline picrate both in salt and in CT-complex modification forms solid solutions with picric acid and bromoaniline. The transition temperature in solid solutions changes from 370 K for PiOH-rich to 377 K for BrA-rich terminal solutions. It is interesting to note that the solubility of BrA is higher in CT-complex phase than in salt phase.

The composition of terminal solutions of BrA in both phases has been evaluated by analysis of heat effects observed at 377 K for samples containing 50–76 mpc of BrA. In Figure 2 heat of transition as estimated from area of the peritectic peak is drawn vs composition. For convenience the composition has been given in mole fraction of picrate in the system: BrA·PiOH ($x = 1$)–BrA ($x = 0$).

If both below and above the peritectic temperature there is only one phase in the system i.e. if a sample contains 50–54 mpc of BrA, the heat of transition of 1 mole of material can be expressed as

$$Q' = x \cdot \Delta H^{\mathrm{tr}} \tag{1}$$

where x is the mole fraction of BrA·PiOH. ΔH^{tr}—molar heat of transition of BrA·PiOH. Here the difference in heat of mixing of *o*-bromoaniline with the two isomers has been neglected.

If there are two phases (salt + liquid) below the transition temperature and only one (solid) above ($\alpha > x > \beta$) one gets by a simple "lever-rule"

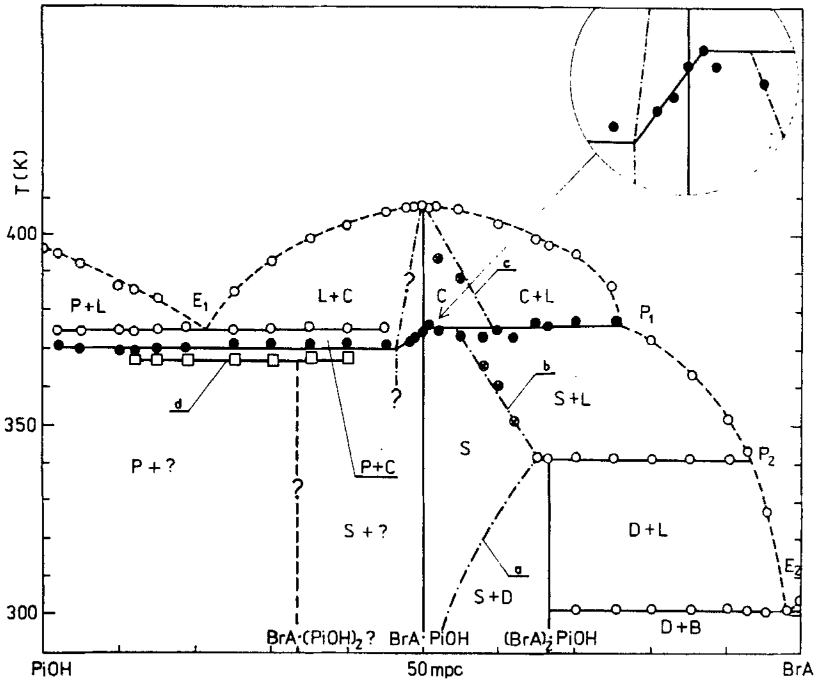

FIGURE 1 Phase diagram of the *o*-bromoaniline–picric acid binary system. Eutectics: E_1 (78 mpc of PiOH), E_2 (less than 2 mpc of PiOH). Peritectics: P_1 (24 mpc of PiOH), P_2 (6.5 mpc of PiOH). P—PiOH, L—liquid, C—solid solution of CT-complex type, S—solid solution of salt type, D—$(BrA)_2PiOH$, B—BrA. --○-- liquidus, —○— eutectic and peritectic lines, —●— salt/complex phase transition, —□— phase transition ?, -·-·-·- boundaries of solid solution region. Insert—the salt/complex transition region in expanded scale.

calculation for the heat of transition

$$Q'' = \frac{x - \gamma}{\alpha - \gamma}\alpha \cdot \Delta H^{\text{tr}} + \frac{\alpha - x}{\alpha - \gamma}\Delta H^{\text{cr}} \tag{2}$$

where α, β, γ are mole fractions of BrA · PiOH in terminal solid solutions of the salt and CT-complex type and in the peritectic liquid respectively (see Figure 2), and ΔH^{cr} is the molar heat of crystallization of the liquid peritectic phase (γ) to CT-complex crystals.

Similarly if solid and liquid phases are present before and after the peritectic transition as well ($\beta > x > \gamma$) one obtains

$$Q''' = \frac{x - \gamma}{\alpha - \gamma}\alpha \cdot \Delta H^{\text{tr}} + \frac{(\alpha - \beta)\cdot(x - \gamma)}{(\alpha - \gamma)\cdot(\beta - \gamma)}\Delta H^{\text{cr}} \tag{3}$$

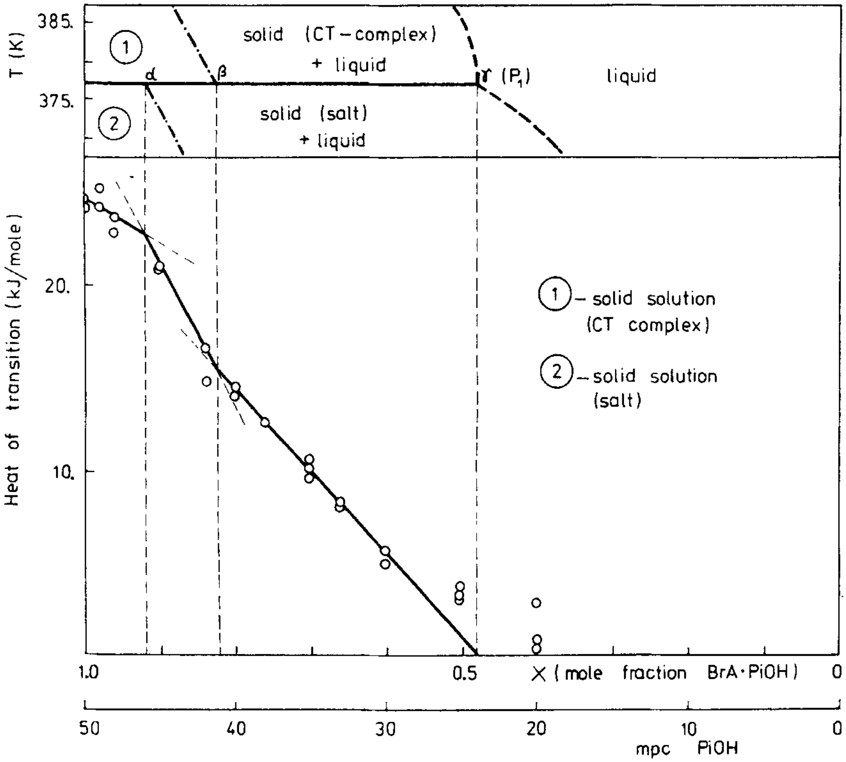

FIGURE 2 Molar heat of transition vs composition of material. The fragment of phase diagram with peritectic line is shown in upper part of figure.

Thus linear relationship between Q and x is expected with slope changing at $x = \alpha$ and $x = \beta$ and equals to

$$\Delta H^{\mathrm{tr}} \quad \text{for } 1 > x > \alpha \tag{i}$$

$$\frac{\alpha \Delta H^{\mathrm{tr}} - \Delta H^{\mathrm{cr}}}{\alpha - \gamma} \quad \text{for } \alpha > x > \beta \tag{ii}$$

and

$$\frac{1}{\alpha - \gamma}\left(\alpha \Delta H^{\mathrm{tr}} + \frac{\alpha - \beta}{\beta - \gamma} \Delta H^{\mathrm{cr}}\right) \quad \text{for } \beta > x > \gamma. \tag{iii}$$

By computational fitting procedure for results given in Figure 2 we have got $\alpha = 0.92$, $\beta = 0.83$, and $\gamma = 0.48$.† From the values and from the value of

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† Results for lowest values of x have been discarded as they are obscured by melting of nonequilibrium solid (cf. p. 340).

slope in intermediate composition range $\Delta H^{cr} = 10.9$ kJ/mole has been evaluated. The slope for $x > \beta$ calculated from (iii) is 46.4 kJ/mole in reasonable agreement with experimental value (48.5 kJ/mole). By this procedure the positions of α-, β-, and γ-points on the peritectic line have been determined more exactly than it would be possible by extrapolation of **b** and **c** lines in the phase diagram. In fact the onset of melting in these samples manifests itself by change of the slope of base line of DTA-curve only and thus could not be determined with reasonable accuracy.

The extent of solubility range of PiOH in BrA·PiOH has not been determined exactly, there is no doubt, however, about existence of solubility between 50 and 52 mpc of PiOH, as eutectic melting was not observed in these samples. Transition temperature for a sample containing 51 mpc of PiOH equals to 373 K and the value is intermediate to that for BrA·PiOH (375 K) and for each sample in which PiOH content exceeds 52 mpc of PiOH (370 K).

$(BrA)_2$·PiOH complex found in this work has not been described hitherto. Its molecular structure has been elucidated by examination of its IR spectrum (Figure 3). The characteristic feature of this spectrum is the presence

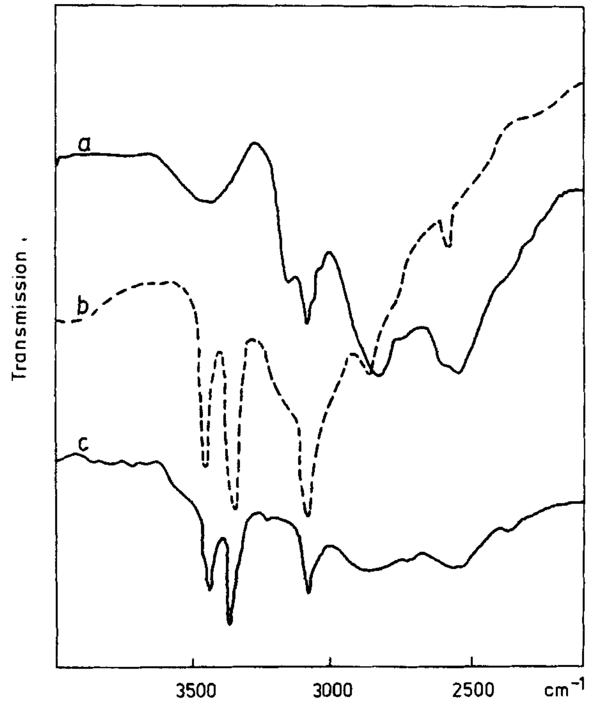

FIGURE 3 IR spectra in KBr wafer. a—BrA·PiOH salt form, b—BrA·PiOH CT-complex form (after Ref. 2), c—$(BrA)_2$·PiOH.

of two sharp vibrational bands at 3375 and 3475 cm^{-1} analogous to those observed in the vibrational spectrum of BrA·PiOH in CT-modification and interpreted there as NH_2-vibrations,[2] beside two broad bands at 2575 and 2825 cm^{-1} identical with those appearing in IR spectrum of BrA·PiOH in salt modification and assigned to NH_3^+-vibrations. Obviously both neutral amine molecule and its cation are present in $(BrA)_2$·PiOH structure. The dark red colour of the compound suggests a CT-interaction. Hence, the structure of the complex may be described as CPT i.e. "charge and proton transfer." This concept has been proposed already by Koffler[13] and it has been applied to similar complexes by Matsunaga.[14] The schema of presumed structure of the CPT-complex $(BrA)_2$ · PiOH is shown in Figure 4.

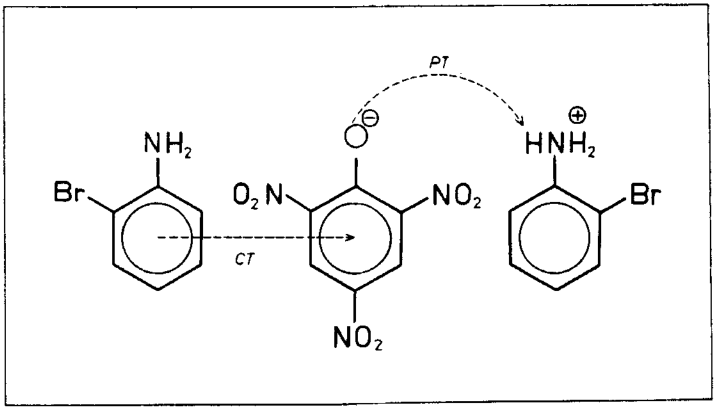

FIGURE 4 Schema of the CPT-complex molecule $(BrA)_2$·PiOH.

The endothermal heat effect observed for samples rich in PiOH in first DTA-run at 367 K (line **d** in Figure 1) might be presumably due to decomposition of a third compound in the system: BrA · $(PiOH)_2$ complex. As we did not succeed in isolation of this compound and in proving its existence by X-ray analysis, and moreover, as the effect was absent in subsequent DTA-runs taken on the same samples, the question of existence of the 1 : 2 compound is still open.

ELECTRIC CONDUCTIVITY

Dc-resistivity of several samples of different composition and its temperature dependence have been also investigated. The relevant results are shown in Figures 5 and 6. The typical sandwich cell with gold electrodes and guard

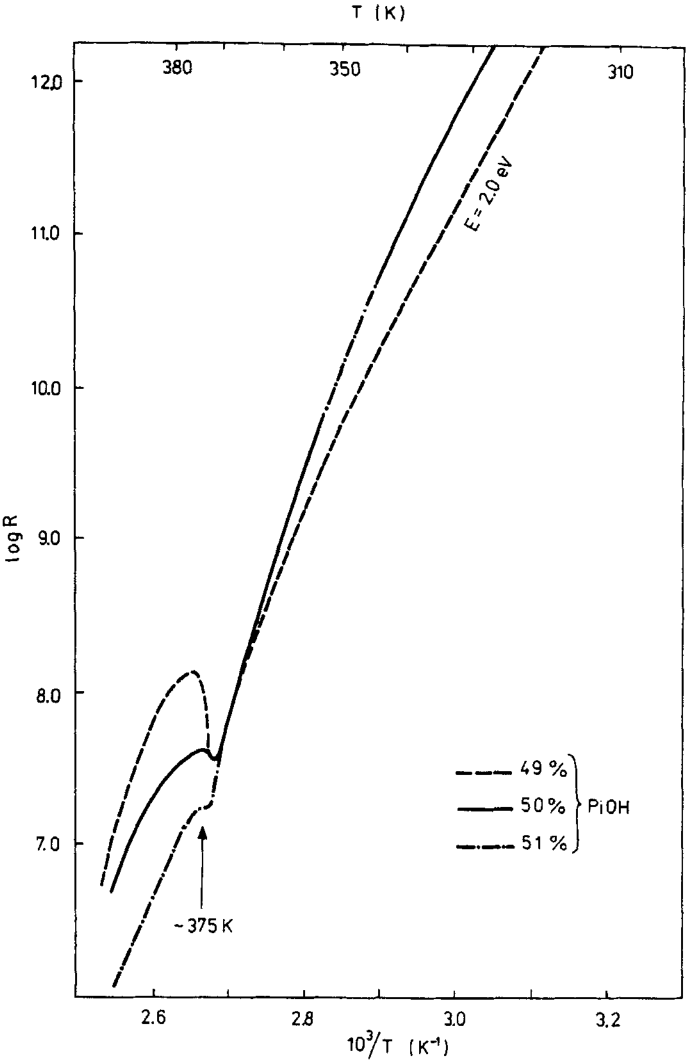

FIGURE 5 Electrical resistivity vs reciprocal temperature measured in solid solution region.

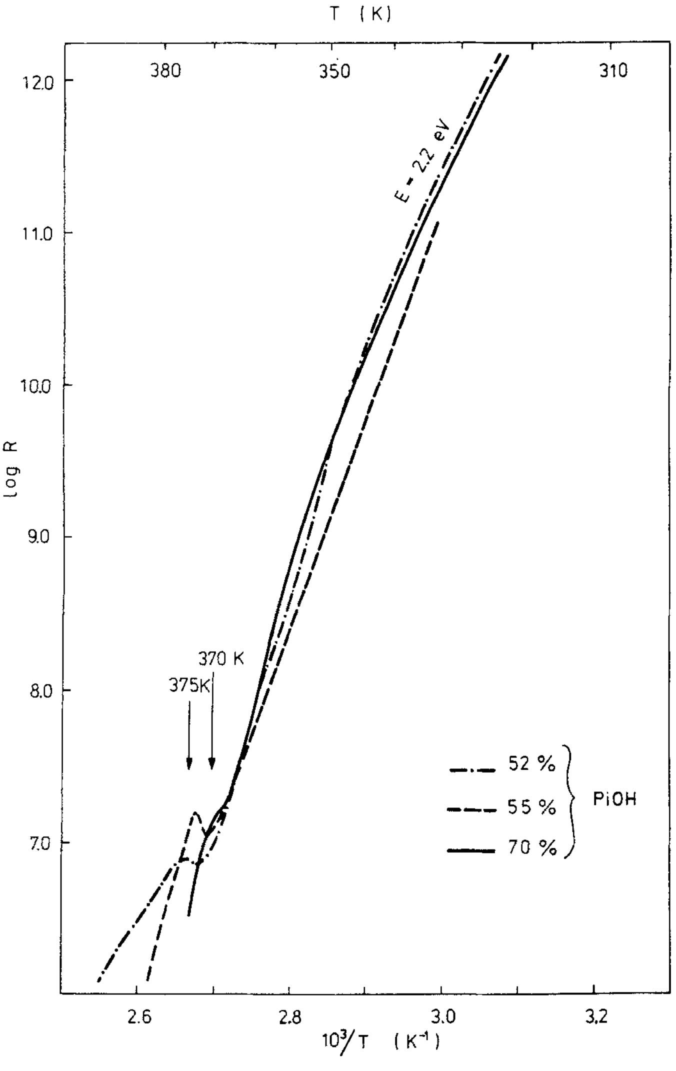

FIGURE 6 Electrical resistivity vs reciprocal temperature for two-phase samples.

ring was used in measurements. In order to watch precisely the resistivity changes in the transition region, electric current flowing through sample was plotted vs time with temperature varying with a constant rate not exceeding 10 deg/h. The resistivity at room temperature for BrA·PiOH is about 10^{14} ohm.cm which is the same as reported by Matsunaga.[2]

The salt/complex phase transition occurring in stoichiometric sample is accompanied by increase in electric resistivity. The same effect is observed in solid solutions, the change being the more pronounced the lower is PiOH content. The onset of eutectic melting in samples containing more than 52 mpc of PiOH is responsible for the sharp decrease in resitivity obscuring the effect of the phase transition. However, the thermal activation energy and resistivity of the samples in salt modification are almost independent of composition as well as of the presence of the second phase.

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