Association and transport properties in solvents of medium and low relative permittivity: Quaternary ammonium picrates in acetone–*n*-hexane mixed solvents

Irina N. Palval, Alexander V. Lebed, Nikolay O. Mchedlov-Petrossyan *

Department of Physical Chemistry, Kharkov V.N. Karazin National University, 61077, Kharkov, Ukraine

ARTICLE INFO

ABSTRACT

The behavior of tetra-*n*-butylammonium picrate, TBAPic, in acetone–*n*-hexane mixed solvent, with the relative permittivity changing gradually from $\varepsilon_r = 20.53$ to 4.99 and only slightly changing viscosity, was studied at 25.0 °C using conductometry. The association constants ($TBA^+ + Pic^- \rightleftharpoons TBA^+Pic^-$, K_A) and the limiting molar conductivities were determined using the Lee–Wheaton equation. At acetone content 50 mass % ($\varepsilon_r = 8.76$) and higher, the 1:1 association model is still able to describe the conductance data at the salt concentrations 3×10^{-5}–0.02 M. These results are in line with the data for some other quaternary ammonium picrates. However, at higher contents of *n*-hexane, this simple model becomes invalid. Therefore, symmetrical ion triplets were involved into the equilibrium scheme. The relation between the mobility of ions and that of the triplets, as calculated conjointly with the equilibrium constants, is close to the common equation: $\Lambda_0^T = 0.693\Lambda_0$. The Walden product $\Lambda_0\eta$, being almost constant up to 50 mass % of acetone, drops at lower ε_r values. The plot of log K_A vs. ε_r^{-1} is linear. However, the K_A value at 27 mass % acetone is 3 times lower as compared with that published earlier for an isodielectric solvent, pure *n*-butylacetate, due to the presence of an "active" dipolar co-solvent. Summarizing of the data for acetone–*n*-hexane system with those for acetone–*n*-butylacetate solutions studied earlier allows concluding that at ε_r around 7, the existence of ion triplets becomes doubtless.

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1. Introduction

In the previous paper [1], the conductance data for tetra-*n*-butylammonium picrate (TBAPic) in acetone–*n*-butylacetate (AC–BA) solvent system at 25 °C have been analyzed. It has been demonstrated, that for this organic electrolyte with relatively poor solvated ions, not inclined to specific interactions, the simple 1:1 ion association model allows to describe adequately the conductance data only at the relative permittivity range $\varepsilon_r > 9$ [1]. The approaches for estimation of the constants of triplets and even quadruplet formation have been developed for lower ε_r values. Ibidem, a brief review of the problem can be found [1].

The aim of the present work was to verify these findings by studying the TBAPic in another solvent system, acetone–*n*-hexane (AC–Hex). The solvents AC and Hex, non-hydrogen bond donors ($E_T^N = 0.355$ and 0.009, respectively [2]), were used to create mixtures with gradually changing ε_r values. The lowest content of AC was 27 mass %. This corresponds to the $\varepsilon_r = 4.99$ value, which is close the $\varepsilon_r = 5.10$ value of pure BA, where the ionic equilibrium of TBAPic was studied previously [1].

The viscosity of this binary mixture stays practically constant. Thus, the alterations of the Walden product (if any) occurring along with ε_r decrease should be ascribed to the decrease in limiting conductivity, Λ_o.

Also, three other alkylammonium picrates were involved in the experimental study.

Finally, we recalculated some well-known precise data on TBAPic conductance in binary organic solvent systems, available in literature, by using the contemporary methods.

2. Experimental section

2.1. Materials

The synthesis, purification, and characterization of TBAPic and tetraethylammonium picrate, TEAPic, was described previously [1]. Cetyltrimethylammonium picrate, CTAPic, was prepared from picric acid (reagent grade, purified by re-crystallization) and cetyltrimethy-lammonium bromide (Merck, purity 99%). The initial reagents with molar ratio 1.12:1 were dissolved in appropriate amount of distilled water; the mixture was heated to 70–80 °C, cooled, stored 20–24 h, and filtrated the precipitate. The dried precipitate was re-crystallized successively from AC and methanol, and dried at 60–80 °C to constant mass. The melting point was 128.3–128.5 °C; elemental analysis: % N calc. 10.93, found 10.90, 10.96; % C calc. 58.57, found 58.65, 58.73; % H

* Corresponding author.
E-mail address: mchedlov@univer.kharkov.ua (N.O. Mchedlov-Petrossyan).

calc. 8.65, found 8.73, 8.73. *N*-cetylpyridinium picrate, CPPic, was prepared from picric acid and *N*-cetylpyridinium chloride (×1 mol H$_2$O, Merck, purity 99%). The initial reagents with molar ratio 1.2:1 were dissolved in appropriate amount of distilled water; the mixture was heated to 50–55 °C, cooled, stored 20–24 h, and filtrated the precipitate. The latter was dried at room temperature and then twice re-crystallized from AC. The salt was dried and stored at room temperature in the desiccator over silicagel. The melting point was 49.2–49.6 and 48.7–49.1 °C, as measured with two samples within a month; elemental analysis: % N calc. 10.52, found 10.47; % C calc. 60.89, found 60.79; % H calc. 7.57, found 7.60.

AC was stored with KMnO$_4$ and after distilling it boiled 4–5 h with dried K$_2$CO$_3$ or MgSO$_4$, again distilled and the middle fraction was used. The reagent grade Hex was purified as described in the literature [2], after making sure of the absence of unsaturated hydrocarbons [3]. After distillation, the middle fraction was collected. The purity of solvents was checked by conductivity and density.

2.2. Apparatus and procedure

Electrical resistance of solutions was measured using an automatic digital AC bridges R5058, R5083 or Precision LCR Meter GW Instek LCR-817 at 25.0 ± 0.05 °C at a frequency of 1000 Hz. Conductance cells were calibrated using a set of aqueous KCl solutions within the concentration range of $c = 2 \times 10^{-4} - 6 \times 10^{-3}$ M.[1] The temperature was maintained with an accuracy of ± 0.05 °C using an aqueous thermostat. The correction for pure solvent conductance was used in the calculations of molar conductance values, Λ; the last-named were obtained with uncertainty of (0.05–0.1) %. The values of relative permittivity, viscosity, and density of pure solvents at 25.0 °C were taken from the literature [4]. The kinematic viscosity of AC–Hex mixtures was determined using a capillary viscosimeter VPZh-2, utilizing freshly distilled water, AC, Hex, and BA as reference liquids. The density of the mixed solvents was measured by picnometric method. All the stock and working solutions were prepared directly before measurements and kept protected from light before measurements.

3. Results

3.1. Physico-chemical properties of mixed solvent

The known literature data [5] on the physico-chemical properties of AC–Hex mixed solvent were compiled together with our experimental data. The interpolated equations were obtained to calculate density (ρ), viscosity (η) and ε_r values of AC–Hex mixtures (see Supplementary data). The values necessary for conductance data processing are gathered in Table 1.

3.2. Conductance data processing

The experimental data on molar conductivities are deposited in the Appendix A: Supplementary data. The phoreograms are typified in Fig. 1.

The main principles of data processing have been described earlier [1]. The extended version of Lee–Wheaton conductance equation [6] and the second approach of Debye–Hückel theory for ionic activity coefficients were used in all calculations. Depending on ε_r value of the solvent, various models of the ion equilibrium can be used. Along with generally known ion association equilibrium,

$$Ct^+ + An^- \rightleftharpoons Ct^+An^-, \quad K_A \tag{1}$$

Table 1
Physico-chemical properties of AC–Hex mixtures at 25 °C.

Content of AC/mass %	ε_r	$10^3 \eta$/Pa s	ρ/g cm^{-3}
100	20.53	0.3030	0.7845
80	15.23	0.2896	0.7505
70	12.88	0.2851	0.7350
60	10.72	0.2818	0.7206
50	8.76	0.2798	0.7071
40	6.99	0.2791	0.6946
27	4.99	0.2804	0.6799

in media with very low polarity ($\varepsilon_r < 10$) the formation of ion triplets becomes possible [7]:

$$Ct^+ + Ct^+An^- \rightleftharpoons Ct^+An^-Ct^+, \quad K_{T+} \tag{2a}$$

$$An^- + Ct^+An^- \rightleftharpoons An^-Ct^+An^-, \quad K_{T-}. \tag{2b}$$

For AC–Hex mixtures with AC content of 80 and 70%, we took into account only the equilibrium [Eq. (1)]; this variant of calculations is designated here as type "A". Therefore, three parameters ($\Lambda_\circ$, K_A and R) were to be fitted in this case. By this type of calculations we also processed the experimental data of Reynolds and Kraus [8] for pure AC. The calculations were successful, but estimation errors of R parameter were considerable in all the cases. Additionally we performed series of testing calculations with two ($\Lambda_\circ$, K_A) fitted parameters and several fixed R values in the range of 0.8–2.0 nm. The results indicated that the influence of R value on the calculation results is negligible, if the body of the experimental data in the series is big enough. Finally, the $\Lambda_\circ$ and K_A values were calculated with the constant value of $R = 1.0$ nm as a mean value for all the above systems.

For AC–Hex mixtures with AC content of 60% ($\varepsilon_r = 10.72$) and less, we used a more complex procedure of data processing (type "B"). As a first step, the preliminary three-parameter ($\Lambda_\circ$, K_A and R) optimization (type "A") was performed using data for the diluted concentration range. Then the formation of ion triplets [Eqs. (2a), (2b)] was taken into account. For simplifying, the assumption $K_{T+} = K_{T-} = K_T$ [7,9] was used. Therefore, only a sole value of the limiting conductivity of triplets ($\Lambda_\circ^T = \Lambda_\circ^{T+} + \Lambda_\circ^{T-}$) can be used. Consequently, four parameters ($\Lambda_\circ$, $\Lambda_\circ^T$, K_A and K_T) were to be fitted, while the value of R parameter was taken from preliminary calculation. The results of
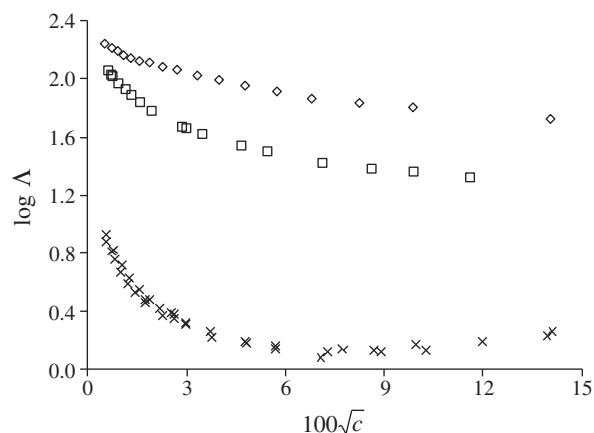

Fig. 1. The dependence of molar conductivities of TBAPic on concentration in AC–Hex mixtures: ◇ − 70 mass % AC; □ − 50 mass % AC; × − 27 mass % AC.