Journal of Molecular Liquids 145 (2009) 158–166

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Association of the picrate ion with cations of various nature in solvents of medium and low relative permittivity. An UV/Vis spectroscopic and conductometric study

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

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

ARTICLE INFO

Available online 17 July 2008

Keywords:
Tetra-n-butylammonium picrate
UV/Vis spectroscopy
Conductance
Ion pairs
Triplets
Quadruples

ABSTRACT

The behavior of tetra-*n*-butylammonium picrate, TBAPic, in acetone–*n*-butyl acetate (AC–BA) solvent system, with the relative permittivity changing gradually from $\varepsilon_r = 20.56$ to 5.10, was studied at 25.0 °C using UV/Vis spectroscopy and conductometry. Interactions of the Pic^- anion with the TBA^+ cation in solution result in changes in its electronic absorption spectrum, though not so markedly as in the case of its association with metal ions, such as Li^+, Na^+, Mg^{2+}, La^{3+}, etc. The association constants ($TBA^+ + Pic^- \rightleftarrows$ ion pair, K_A) and the limiting molar conductivities were determined using the Lee–Wheaton equation. The literature K_A value in pure AC is refined. The state of TBAPic, an electrolyte with relatively poor solvated cations and anions, in solvents of medium and low polarity is discussed. At an AC content of 25 mass % and less, the 1:1 association model is unable to satisfactorily describe the conductance data. Hojo's method, modified to some extent by us, was used to fit the phoreograms by taking into consideration symmetrical ion triplets and quadruples, with equilibrium constants K_T and K_Q, respectively. Our approach presumes also the possible extrapolation of the plots of the Walden product logarithm, $\log(\Lambda_o \eta)$, as well as that of $\log K_A$ vs. ε_r^{-1} to required low ε_r value. This allows to refine the Λ_o value for pure BA and to verify the K_A value estimated by Hojo's procedure in this solvent.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Ion association between cations and anions [Eq. (1)] is known to control the ionic processes in media of medium and low polarity, e.g., in solvents with a relative permittivity, ε_r, below ca. 20–30 [1–9].

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

The role of non-specific association can be observed first of all by studying the behavior of true electrolytes, or ionophores [2,9], especially in the case of poor solvating solvents, which are unable to act as hydrogen-bond donors. Conductance studies serve as a universal method of determination of corresponding equilibrium constants. In several cases, UV/Vis spectroscopy can be also applicable for the same purpose.

In media with very low ε_r values ($\varepsilon_r < 10$), two general problems arise. First, the possibility of stepwise ionic association has to be taken into account, even in the absence of specific cation/anion interactions. Fuoss and Kraus [1,2,10] introduced the model of ion triplets formation and in such a way explained the molar conductivity minimum in solvents with low ε_r values. Moreover, at high concentrations of the electrolyte, the formation of ion quadruples or even more complicated species is possible [3,4,8,11–14], Eqs. (2a), (2b), (3), (4).

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

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

$$2Ct^+An^- \rightleftarrows (Ct^+An^-)_2, \quad K_Q \tag{3}$$

$$nCt^+An^- \rightleftarrows (Ct^+An^-)_n, \quad K_N \tag{4}$$

The second problem consists in the estimation of limiting molar conductivities of charged species (or some of them). One way is to calculate these values as optimized parameters together with equilibrium constants during the fitting procedure, but there are many mathematical difficulties in this way. Otherwise, it is possible to obtain these values by some additional approaches (for instance, using Walden's rule). In this case, only equilibrium constants are the parameters to be calculated.

Contrary to the concept developed by Fuoss and Kraus [10], some authors demonstrated that the molar conductivity minimum can be

---

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

0167-7322/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.molliq.2008.07.006

explained using only the simple association scheme given in Eq. (1) [15]. Sukhotin [15a,b] took into account the activity coefficients and the alteration of ε_r of the solvent in the presence of the electrolyte; Weingärtner, Weiss, and Schröer [15c] involved into consideration various models of ion–ion pair interactions without triplets formation.

Usually, the constants K_{T+} and K_{T-} are supposed to be equal to each other [1,2,10,14,16]. Alternatively, Lindbäck and Beronius [17] managed to describe the conductance data of tetra-*n*-propylammonium picrate in chlorobenzene by using only Eqs. (1) and (2b). The state of the art in this field was reflected in excellent papers of Salomon and Uchiyama [16], Abbott and Schiffrin [18] (the last-named authors actually introduced the concept of penetrated ion pairs), and Petrucci and Eyring [19], who proposed to estimate the activity coefficients of ion associates. A set of fundamental papers of Barthel and co-workers [20] should be also mentioned here. Within the recent decade, Hojo and co-workers [14b,21] demonstrated that, using some reasonable assumptions, it is possible to evaluate all the above-mentioned constants (K_A, K_T, and K_Q). Recently, Holovko [22] gave some examples of processing conductance data in terms of various ion associates. Consequently, the plurality of possible approaches should be taken into consideration by the interpretation of experimental results.

Finally, at high concentrations of the electrolyte and/or high temperature, the term ‘ion association’ in low-permittivity media is somewhat conventional [23]. Hence, application of the mass action law approach is conditional in this case.

Taking into account the multiplicity of ion associates (not only contact, or tight, and solvent-separated or loose, but also penetrated ones, as well as those with H-bonds, etc.), we decided to consider the behavior of tetra-*n*-butylammonium picrate, TBAPic, in solution as a representative example for the solvent-dependence of ion association. In this case, specific interactions between cation and anion seem to be improbable. A lot of publications were devoted to thermodynamic properties of this electrolyte in organic solvents [4,8,12,13,24–28]. Nowadays, it is also used in studies of systems near the critical consolute point [29,30].

On the other hand, the UV/Vis absorption spectrum of the picrate ions is known to display more or less expressed changes resulting from its association with some counter-ions such as metal cations [31–33], their crown complexes [34], and hydrogen-bond donors of R_3NH^+ type [35]. We determined the equilibrium constant of 0.74±0.14 for the exchange reaction ($TBA^+Pic^- + Na^+DS^- \rightleftarrows Na^+Pic^- + TBA^+DS^-$, DS^- is *n*-dodecyl sulfate) in the solvent mixture toluene+2-propanol (mass ratio 4 : 1, $\varepsilon_r = 3.59$) by an UV/Vis spectroscopic method [36].

According to the accepted point of view, conductance data allow to obtain the overall equilibrium constant for the association between free ions and all kinds of ion pairs (loose, tight, penetrated, etc.) [3,9]. The situation becomes less clear with UV/Vis spectroscopic measurements. In some cases it has been found that ions in loose pairs exhibit light absorption equal to that of free ions [3,9]. Evidently, this depends strongly on the sensitivity of the given chromophore to any disturbances in its environment. Moreover, in solvents with medium ε_r values, spectral changes caused by the ‘field effect’ of counter-ions without association cannot be excluded.

Kendrick and Gilkerson [37b] demonstrated that the association constants of Pic^- with lithium and sodium ions in 2-propanol practically coincide as determined by both experimental methods. Thus, it is significant to clarify if such coincidence will take place in the case of picrate association with tetraalkylammonium cations. As a rule, coincidence of the UV/Vis spectra of free Pic^- ions with that of its associate with such pseudo-spherical counter-ions is implied. The sole exception known to us is the study of Gilkerson and Kendrick [38b].

The aim of our work is to reveal the possibilities of UV/Vis spectroscopic estimation of the association constant K_A ($TBA^+ + Pic^- \rightleftarrows TBA^+Pic^-$) and to examine Hojo's approach to processing the conductance data, somewhat modified by us, to the treatment of association equilibria in media of low polarity. Acetone (AC) and *n*-butyl acetate (BA), protophobic ($DN^N = 0.438$ and 0.284, respectively) non-hydrogen-bond donors ($E_T^N = 0.355$ and 0.241, respectively) were used to create mixtures with a relative permittivity changing gradually from $\varepsilon_r = 20.56$ to 5.10. Some UV/Vis spectroscopic experiments were done also with tetraethylammonium picrate, TEAPic; *iso*-butyl acetate, *iso*-BA, was used instead of BA in several cases. Finally, it seemed to be worthwhile to reveal, what changes the Pic^- absorption spectrum can undergo on introducing multi-charged cations.

2. Experimental section

2.1. Materials

TBAPic was synthesized from picric acid and tetra-*n*-butylammonium iodide (25% excess) in water. The mixture was stored one day, the deposit was filtered off, recrystallized from methanol or ethanol, and dried to constant mass at 60–70 °C. Recrystallization from acetone gives low yields, while using benzene results in stratification of the solution, in accord with literature data [39]. Melting point was 89.2–89.6 °C; literature: 89.8–90.1 °C [40], 89.5 °C [41], 91 °C [42]; elemental analysis: % N calc. 11.90, found 12.02, 12.07. Two series of experiments carried out with independently prepared samples of the salt demonstrated identical results. The sample of tetraethylammonium picrate of high purity was additionally recrystallized from methanol and dried to constant mass at 60–90 °C. Its melting point was 258.2–258.3 °C; literature: 259–261 °C [40a], 255.8 °C [41], 260–261 °C [42]; elemental analysis: % N calc. 15.63, found 15.66, 15.68.

The reagent grade samples of lithium and sodium perchlorate were used as received, while the sample of $Mg(ClO_4)_2 \times 6H_2O$ was dried to constant mass at 120–125 °C. Samples of $La(NO_3)_3 \times 6H_2O$, $Ho(NO_3)_3 \times 6H_2O$, and $Th(NO_3)_4$ were gifted to us by Dr. T. A. Shakhverdov, St-Petersburg, and used as such. The sample of dicyclohexyl-18-crown-6, *cis–anti–cis* (isomer B) was purchased from the Institute of General and Inorganic Chemistry, Russian Acad. Sci., Moscow. AC was stored with $KMnO_4$ and after distilling it was boiled 4–5 h with dried K_2CO_3 or $MgSO_4$, again distilled and the middle fraction was used. BA and *iso*-BA were boiled for 4–5 h with dried $MgSO_4$, distilled and the middle fraction was used. The purity of solvents was checked by conductivity and density.

2.2. Apparatus and procedure

UV/Vis absorption spectra were run at 25.0±0.5 °C on SF-26 or SF-46 apparatus, against solvent blanks; some measurements were done at room temperature. A set of cuvettes (0.1, 1.0, and 5.0 cm) was used for working within the absorbance range of 0.3 to 1.3.

Resistance of solutions was measured using an automatic digital ac bridge R5058 (with the limit of main error 0.2%) at 25.0 °C at a frequency of 1000 Hz. Conductance cells were calibrated using a set of aqueous KCl solutions within the concentration range of $c = 2 \times 10^{-4}$–6×10^{-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 an accuracy of (0.5–1) %.

The ε_r values were taken from the literature or determined at 25.0 °C by the dielcometer ON-301, using BA ($\varepsilon_r = 5.10$) and dichloromethane ($\varepsilon_r = 8.93$) for the calibration of the cells; the measurements were done in the Research Institute for Chemistry at Kharkov National University. The kinematic viscosity of solvents was determined using the capillary viscosimeter VPZh-2, utilizing freshly distilled water, acetone, *n*-hexane, and BA. The data were converted to dynamic viscosities by using density values.

All the stock and working solutions were prepared directly before measurements and kept protected from light before measurements.

---

[1] 1 M=1 mol dm^{-3}.

Download English Version:

https://daneshyari.com/en/article/5413281

Download Persian Version:

https://daneshyari.com/article/5413281

Daneshyari.com