MOBILITIES OF SOME UNIVALENT IONS IN AQUEOUS AND NITROBENZENE MEDIA

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Limiting ionic equivalent conductivities of selected univalent ions in water, nitrobenzene, or water–saturated nitrobenzene were taken or calculated from literature data. Based on previous conductivity measurements, it was shown that the proton mobility in nitrobenzene saturated with water is comparable with that of alkali metal ions.

Nitrobenzene, a dipolar aprotic solvent, has frequently been used in solution extraction, especially in the separation of caesium, strontium, and radium from aqueous solutions[1–3]. Recently, a considerable attention has been paid to the study of charge transfer through the water–nitrobenzene interface[4]. Nitrobenzene is also suitable for accurate conductimetric measurements.

The aim of the present work was to determine the limiting ionic equivalent conductivities of some univalent ions in nitrobenzene saturated with water.

RESULTS AND DISCUSSION

The limiting ionic equivalent conductivity λ_i^0 in a given solvent gives some information about ion solvation and effective size of moving ions including the solvation sphere, which depends mainly on the energy of ion–solvent interaction and on the size of the solvent molecule. Owing to difficulties in application of standard methods for the determination of transference numbers of ions in nonaqueous solvents, the determination of limiting ionic equivalent condutivities of individual ions requires to introduce a certain assumption according to which the limiting equivalent conductivity of a salt solution can be splitted into the contributions of individual ions. Thus, *e.g.* the limiting ionic equivalent conductivities λ_i^0 of certain ions in pure nitrobenzene summarized in Table I were calculated on the assumption that the limiting equivalent conductivities of tetraisoamylammonium cation and tetraisoamylborate anion are equal to each other[10].

Škarda and coworkers[5,6] have shown on the basis of conductivity measurements that salts of the type $M^+[(1,2\text{-}C_2B_9H_{11})_2Co]^-$, where M^+ is an alkali metal cation,

Tl^+, or $N(C_2H_5)_4^+$, and the other ion is hydrophobic polyhedral dicarbollylcobaltate anion (abbreviation DCC^-), in nitrobenzene saturated with water are fully dissociated. Moreover, they determined the hydration numbers of the mentioned cations indicating the mean number of water molecules bound to them in the given medium, however, they did not determine the limiting ionic equivalent conductivities.

The latter values for certain univalent ions in nitrobenzene saturated with water can be simply obtained from the results of the mentioned authors as follows. The measured dependences of the equivalent conductivity Λ on $\sqrt{c}$, where c denotes the concentration of the salt MDCC in nitrobenzene exctracts[5,6], can be extrapolated to give the following limiting equivalent conductivities:

$$\Lambda^0_{(LiDCC)} = 24{\cdot}8\,, \quad \Lambda^0_{(HDCC)} = 25{\cdot}5\,, \quad \Lambda^0_{(NaDCC)} = 26{\cdot}9\,,$$

$$\Lambda^0_{(KDCC)} = 29{\cdot}3\,, \quad \Lambda^0_{(N(C_2H_5)_4DCC)} = 29{\cdot}8\,, \quad \Lambda^0_{(TlDCC)} = 31{\cdot}0\,,$$

$$\Lambda^0_{(CsDCC)} = 32{\cdot}2\,, \quad \Lambda^0_{(RbDCC)} = 33{\cdot}0\ \Omega^{-1}\ cm^2\ mol^{-1}\,.$$

Using the law of Kohlrausch about independent mobility of ions at infinite dilution, which in our case can be written as

$$\Lambda^0_{(MDCC)} = \lambda^0_{(M^+)} + \lambda^0_{(DCC^-)}\,, \qquad (1)$$

the value of $\Lambda^0_{(N(C_2H_5)_4DCC)} = 29{\cdot}8\ \Omega^{-1}\ cm^2\ mol^{-1}$, and assuming that the limiting equivalent conductivity of the $N(C_2H_5)_4^+$ cation in "dry" nitrobenzene is the same as in nitrobenzene saturated with water* ($\lambda^0_{(N(C_2H_5)_4^+)} = 16{\cdot}1\ \Omega^{-1}\ cm^2\ mol^{-1}$ according to ref.[9,10]), we obtain $\lambda^0_{(DCC^-)} = 13{\cdot}7\ \Omega^{-1}\ cm^2\ mol^{-1}$. The values for the other cations are then calculated from extrapolated values of $\Lambda^0_{(MDCC)}$ and the value of $\lambda^0_{(DCC^-)}$ by Eq. (*1*). The results are given in Table I along with some data about λ^0_i for different ions in "dry" nitrobenzene and in water taken from the literature.

It is seen from Table I that the limiting equivalent conductivities of certain univalent cations in water and in nitrobenzene saturated with water increase in the sequence $\lambda^0_{(Li^+)}$, $\lambda^0_{(Na^+)}$, $\lambda^0_{(K^+)}$, $\lambda^0_{(Tl^+)}$, $\lambda^0_{(Cs^+)}$, $\lambda^0_{(Rb^+)}$. This is very probably related to decreasing effective radius of the moving solvated ions in both media. The somewhat decreasing mobility of the solvated Na^+ and K^+ ions on passing from "dry" to "wet" nitrobenzene (Table I) can be discussed analogously (the solvation sphere of alkali metal cations in water-saturated nitrobenzene contains water molecules whose mean number is characterized by the hydration numbers[5,6]).

* This is justified by the fact that $N(C_2H_5)_4^+$ cations are not hydrated in nitrobenzene saturated with water[5,6], hence their effective radius in "dry" nitrobenzene is considered equal to that in water-saturated nitrobenzene (containing only 0·16 mol l^{-1} H_2O, ref.[6]).

It is remarkable that the quantity $\lambda^0_{(H^+)} = 11{\cdot}8\ \Omega^{-1}\,cm^2\,mol^{-1}$ is comparable with limiting equivalent conductivities of alkali metal cations and tetraethylammonium cation in water-saturated nitrobenzene (Table I), whereas in aqueous medium the mobility of hydrated protons is several times higher than that of other ions. Thus, it seems that the mechanisms of transfer of the solvated protons and solvated alkali metal cations in water-saturated nitrobenzene are essentially the same. The very high mobility of protons in water is explained by the well-known theory of proton jump between neighbouring water molecules (Grotthus mechanism).

The standard Galvani potential difference between two immiscible liquids is one of the most important quantities characterizing reversible ion transfer across interface between the mentioned liquids[4]. The values of the Galvani potential differences for a univalent cation M^+ and anion A^- between nitrobenzene (nb) and water (w) phases, denoted as $\Delta^{nb}_w\varphi^0_{M^+}$ and $\Delta^{nb}_w\varphi^0_{A^-}$, can be calculated from the polarographic half-wave potentials, $(\Delta^{nb}_w\varphi_{M^+})_{1/2}$ and $(\Delta^{nb}_w\varphi_{A^-})_{1/2}$, corresponding to reversible

TABLE I

Limiting equivalent conductivities λ^0_i ($\Omega^{-1}\,cm^2\,mol^{-1}$) of univalent ions at 25°C in nitrobenzene(1), nitrobenzene saturated with water(2), and water(3)

Ion	λ^0_i(1)	Ref.	λ^0_i(2)	Ref.	λ^0_i(3)	Ref.
Li^+	—	—	11·1	present work	$38{\cdot}6_8$	12, 21
H^+	—	—	11·8	present work	$349{\cdot}8_1$	11, 12, 21
Na^+	16·02	8, 10	13·2	present work	50·10	12, 13, 21
K^+	17·53	8, 10	15·6	present work	73·50	13, 14, 21
Tl^+	—	—	17·3	present work	74·7	16, 21
Cs^+	—	—	18·5	present work	$77{\cdot}2_6$	15, 21
Rb^+	—	—	19·3	present work	$77{\cdot}8_1$	15, 21
NH_3^+	18·12	8, 10	—	—	$73{\cdot}5_5$	17, 21
$N(CH_3)_4^+$	17·0	9, 10	—	—	$44{\cdot}9_2$	18, 21
$N(C_2H_5)_4^+$	16·1	9, 10	16·1	9,10	$32{\cdot}6_6$	18, 21
$N(C_3H_7)_4^+$	13·2	9, 10	—	—	$23{\cdot}4_2$	18, 21
$N(C_4H_9)_4^+$	11·55	7, 10	—	—	$19{\cdot}4_7$	18, 21
Cl^-	22·68	8, 10	—	—	76·35	13, 14, 21
Br^-	21·93	8, 10	—	—	78·14	13, 14, 21
J^-	21·25	7, 10	—	—	$76{\cdot}8_4$	14, 21
NO_3^-	22·79	7, 10	—	—	71·46	12, 21
ClO_4^-	17·7	8, 10	—	—	$67{\cdot}3_6$	19, 21
CH_3COO^-	23·95	8, 10	—	—	$40{\cdot}9_0$	20, 21
Picrate	16·28	7, 10	—	—	30·39	18, 21
$B(C_6H_5)_4^-$	10·79	7, 10	—	—	—	—
DCC^-	—	—	13·7	present work	—	—

transfer of these ions between the two phases[22]

$$\Delta_w^{nb}\varphi_{M^+}^0 = (\Delta_w^{nb}\varphi_{M^+})_{1/2} + (RT/2F)\ln[D_{M^+}(w)/D_{M^+}(nb)], \quad (2)$$

$$\Delta_w^{nb}\varphi_{A^-}^0 = (\Delta_w^{nb}\varphi_{A^-})_{1/2} + (RT/2F)\ln[D_{A^-}(nb)/D_{A^-}(w)]. \quad (3)$$

Here, $D_{M^+}(w)$, $D_{M^+}(nb)$, $D_{A^-}(w)$, and $D_{A^-}(nb)$ denote diffusion coefficients of M^+ and A^- ions in water and nitrobenzene. The above equations apply only if both phases contain a sufficient excess of a base electrolyte[4], so that the migration current can be neglected, and that the molar activity coefficients of M^+ and A^- ions in water and nitrobenzene satisfy the relations $\gamma_{M^+}(w)/\gamma_{M^+}(nb) = \gamma_{A^-}(w)/\gamma_{A^-}(nb) = 1$.

We set approximately $D_{M^+}(w)/D_{M^+}(nb) \approx D_{M^+}^0(w)/D_{M^+}^0(nb)$, $D_{A^-}(nb)/D_{A^-}(w) \approx \approx D_{A^-}^0(nb)/D_{A^-}^0(w)$, where the superscript 0 refers to infinite dilution, and use the Nernst–Einstein relation[23]

$$D_{M^+}^0 = (RT/F^2)\lambda_{M^+}^0, \quad D_{A^-}^0 = (RT/F^2)\lambda_{A^-}^0. \quad (4), (5)$$

Then, equations (2) and (3) can be rewritten in the form

$$\Delta_w^{nb}\varphi_{M^+} = (\Delta_w^{nb}\varphi_{M^+})_{1/2} + (RT/2F)\ln[\lambda_{M^+}^0(w)/\lambda_{M^+}^0(nb)], \quad (6)$$

$$\Delta_w^{nb}\varphi_{A^-}^0 = (\Delta_w^{nb}\varphi_{A^-})_{1/2} + (RT/2F)\ln[\lambda_{A^-}^0(nb)/\lambda_{A^-}^0(w)]. \quad (7)$$

Samec and coworkers have shown[24] that the ratio of the diffusion coefficients of ferrocene in nitrobenzene and acetonitrile is approximately equal to the ratio of the viscosities of acetonitrile and nitrobenzene. In analogy, we should expect that $\lambda_i^0(w)/\lambda_i^0(nb) = \eta_{nb}/\eta_w$ (η_{nb} and η_w denote the viscosities of nitrobenzene and water). This relation is best satisfied by tetraethylammonium and picrate ions (Table I) or, to a lesser degree of accuracy, by $N(C_3H_7)_4^+$, $N(C_4H_9)_4^+$, and $CH_3.COO^-$ ions. For most of the remaining ions in Table I, the error in determining $\Delta_w^{nb}\varphi_{M^+}^0$ and $\Delta_w^{nb}\varphi_{A^-}^0$ from the polarographic half-wave potentials for reversible ion transfer through the water–nitrobenzene interface would be too large owing to inaccuracy in the mentioned (Walden's) rule. At 25°C, the error would be in the range 5–11 mV provided that equations (6) and (7) are accurate enough. For $N(CH_3)_4^+$ ions, the error would be only 3 mV, whereas for hydrogen ions it would be as high as 34 mV.

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