PHYSICO-CHEMICAL STUDIES IN LOW DIELECTRIC SOLVENTS: PART II. IONIC B-COEFFICIENTS IN N-BUTANOL

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Relative viscosities of some 1:1 electrolytes are reported in n-butanol at 25°C. Viscosity coefficient of Jones-Dole equation have been evaluated and all electrolytes are found to behave as structure makers in this solvents. Ionic B-coefficients have been evaluated by the method suggested by Krumgalz. Variation of ionic B-coefficient with the size of the ions in this solvents is in accord with that in other solvents. In order to throw light on ion-solvent interactions, solvation numbers of the ions have also been computed using Einstein's equation and ionic B-coefficients.

In a previous (part I) paper[1] we reported the viscosity B-coefficients for some electrolytes in n-butanol using the Jones-Dole equation[2].

The detailed information about the ion-solvent interactions can be obtained only if the B-values are dividied into the individual ionic contributions. The viscosity measurements in n-butanol have, here, been extended to include a few more salts to provide a basis for splitting the B-coefficients of the electrolytes into the ionic contributions.

EXPERIMENTAL

n-butanol (BDH AnalaR) was purified as reported earlier [1]. Sodium iodide (BDH AnalaR) and the tetraalyklammonium salts (Fluka AG) were crystalysed from conductivity water and dried in vaccum at 100 °C.

All the solutions were made by weight under dry conditions. Conversion between molality and molarity was done as dicussed[1].

Viscosity of the solutions was measured by using a modified Ubbelohde capillary type viscometer as reported earlier[1]. Density of the solutions of different concentrations have been mesured with the help of a bicapillary pycnometer.

RESULTS AND DISCUSSION

Viscosity and density of sodium iodide, tetraethylammonium chloride, tetrabutylammonium chloride, tetrabutylammonium bromide, tetrabutylammonium iodide and sodium tetraphenylborate have been measured in the concentration range of 0.96 to 30.10 x 10^{-3} mol litre^{-1} at 25°C in n-butanol. All the relevant data are recorded in Table 1.

TABLE 1

VISCOSITY DATA OF SOME 1:1 ELECTROLYTE IN N-BUTANOL AT 25°C

Electrolyte	Conc (mol/litre)	d (g/ml)	η_r
NaI	0.00151	0.8058	1.0063
	0.00263	0.8062	1.0093
	0.00614	0.8069	1.0175
	0.00801	0.8072	1.0219
	0.01041	0.8077	1.0265
Et_4NCl	0.00261	0.8059	1.0030
	0.00452	0.8061	1.0047
	0.00762	0.8064	1.0073
	0.01412	0.8070	1.0126
	0.02043	0.8072	1.0173
Bu_4NCl	0.00096	0.8071	1.0045
	0.00428	0.8074	1.0116
	0.01801	0.8088	1.0328
	0.02683	0.8092	1.0453
Bu_4NBr	0.00232	0.8061	1.0056
	0.00581	0.8064	0.0119
	0.00960	0.8068	1.0172
	0.01205	0.8070	1.0208
	0.01361	0.8074	1.0223
Bu_4NI	0.00118	0.8059	1.0029
	0.00391	0.8062	1.0075
	0.00472	0.8064	1.0086
	0.00509	0.8067	1.0091
	0.00717	0.8068	1.0113
	0.00941	0.8072	1.0151
	0.01236	0.8077	1.0186
$NaBPh_4$	0.00262	0.8064	1.0175
	0.00442	0.8074	1.0245
	0.01266	0.8085	1.0508
	0.02010	0.8097	1.0713
	0.02737	0.8103	1.0915

The viscosity data have been analysed by the Jones-Dole equation[1]. A and B parameters have been evaluated from the linear plots of $(\eta/\eta_0 - 1)/\sqrt{c}$ versus $\sqrt{c}$ and are recorded in Table 2.

TABLE 2

VALUES OF PARAMETERS OF JONES-DOLE EQUATION IN N-BUTANOL

Electrolyte	A (mole$^{-1/2}$ litre$^{1/2}$)	B (mole^{-1} litre)
NaI	0.093	1.43
Et Cl	0.024	0.70
Bu NCl	0.088	1.11
Bu NBr	0.065	1.05
Bu NI	0.052	1.02
NaBPh	0.026	1.83

Comparison of B-coefficient in n-butanol with those in methanol and ethanol reveals that the values in n-butanol are higher[3-5].

B-coefficients so obtained are the sum of contributions from the cationic and anionic species in solution towards ion-solvent interactions. In order to know the contributions due to cations and anions, the B-coefficients need to be divided into the constituting ions of the salts. Krumgalz[6] proposed a method for the division of B-coefficients by assuming that B coefficients of large tetraalkylammonium ions, which are not solvated in solution are proportional to the cube of their stokes radii:

$$\frac{B_{Bu_4N^+}}{B_{Et_4N^+}} = \frac{r^3_{Bu_4N^+}}{r^3_{Et_4N^+}} \quad \ldots\ldots\ldots (2)$$

The stokes radii of the ions are related to the limiting equivalent ionic conductances as follows[7].

$$r_i = F^2|Z_\pm| \Big/ 6\pi\eta_0 N\lambda^\circ_\pm \quad \ldots\ldots\ldots(3)$$

All the symbols have their usual meanings(7). Equation(2) can thus be written as:

$$\frac{B_{Bu_4N^+}}{B_{Et_4N^+}} = \left[\frac{\lambda^0_{Et_4N^+}}{\lambda^0_{Bu_4N^+}}\right] \quad \ldots\ldots\ldots (4)$$

Since B-coefficients of the salt is the sum of the ionic contributions,

$$B_{Bu_4N^+} - B_{Et_4N^+} = B_{Bu_4NCl} - B_{Et_4NCl} \quad \ldots\ldots(5)$$

The values of limiting equivalent ionic conductances have been taken from literature[8,9]. B-coefficients of Bu_4N^+ and Et_4N^+ ions have been determined using equations 4 and 5 and those of the other ions have been determined assuming it to be an additive property. The ionic B-coefficients are recorded in Table-3.

TABLE 3

VARIOUS IONIC PARAMETERS FROM VISCOSITY DATA IN N-BUTANOL

Ion	$B_\pm$ (mol^{-1} litre)	r_s (A)	r_{covr} (A)	n_B	n_{λ°
Na^+	1.13	4.72	5.52	4.55	-
*K^+	0.96	4.49	5.36	4.05	-
*NH_4^+	0.92	4.41	5.09	3.59	4.53
*Me_4N^+	0.15	2.43	3.47	-	-
Et_4N^+	0.31	3.09	4.00	-	-
Bu_4N^+	0.72	4.06	4.97	-	-
Cl^-	0.39	3.37	4.28	2.01	3.85
Br^-	0.33	3.22	4.14	1.78	3.11
I^-	0.30	3.06	3.98	1.51	2.28
*SCN^-	0.29	3.04	3.96	1.48	-
Ph_4B^-	0.70	4.03	4.80	-	-

** Reference 4.
* Calculated from reference 1.

Persual of Table 3 reveals that the ionic B-coefficients of alkali metal and halide ions decrease with increase in the size of the ions and that of tetraalkylammonium ions increase with the increase in the size of the ions. This is in accord with the findings in various solvents [3-6, 10,11].

When an electrolyte dissolves in a solvent, some of the solvent molecules are attached to the ions due to the ion-solvent interactions and this results in the increase in viscosity of solution (positive contribution towards B-coefficients). On the other hand, these solvent molecules have to dissociate from the bulk solvent and this distruction of the solvent structure results in the decrease in viscosity of the solution (negative contribution towards B-coefficients). The value of B-coefficients in a solvent is thus the resultant of these two opposing factors. In methanol, ethanol and n-butanol, the contribution due to the first factor can be expected to be almost the same; that of the second one will decrease with increase in molecular weight of the alcohols as the higher alcohols are less structured. Thus the higher values of B-coefficients in n-buthanol are in line with the Hydrogen bondings in these solvents. So the ionic B-coefficients can be taken as due to the size factor only.

In order to get some quantitative information about ion-solvent interactions, ionic B-coefficients have been used to compute solvation

numbers of the ions using equation[7] obtained by combining Jones-Dole equation and Einstein's equation(10,12).

$$B_{\pm} = \frac{2.5}{1000} (V_i + n_B V_S) \quad \ldots\ldots(6)$$

Where, V_i is the molar volume of the bare ion,
V_S is the molar volume of solvent and
n_B is primary solvation number of the ion.

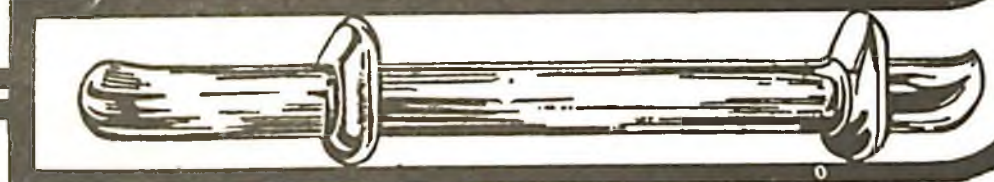
Solvation numbers of the ions have been calculated after applying the correction suggested by Nightingale[13]. All the relevant data alongwith the solvation numbers of the ions ($n_{\lambda 0}$) obtained from the conductance data[8] are recorded in Table-3.

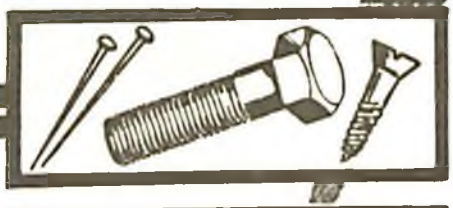
Examination of Table-3 reveals that solvation numbers obtained from the viscosity data are less than those obtained from conductivety data, though both the methods are supposed to give primary solvation numbers. However, it is an established fact that the solvation numbers obtained by different methods differ from each other as the various techniques determine the size of the solvated ion under different surroundings[14].

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