

1090 and 985 J mol⁻¹ in the case *n*-, *iso*-, *sec*- and *tert*-butanols respectively. The above trend agrees well with Brown's observations⁶ in case of binary mixtures of isomeric butanols with benzene. It is clear from above results that there is a pronounced effect on G^E due to branching to alkyl chain in isomeric butanols. At present it is not possible to interpret the data as we have yet to measure the enthalpy and entropy of mixing for all systems.

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Physico-chemical Studies in Non-aqueous Solvents: Part XIX—Viscosity Studies of Some 1:1 Electrolytes in Tetramethylurea

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Viscosities of some alkali metal salts and ammonium perchlorate have been measured in the concentration range 3.2-128.2 × 10⁻³ mol litre⁻¹ at 25° in tetramethylurea. The data have been analysed by the Jones-Dole equation. The viscosity *B* coefficients for all the electrolytes are positive and found to decrease with increasing size of the cation (except for NH₄⁺ ion).

VISCOSITY measurements have been found to be useful in elucidating¹⁻³ the structures of electrolyte solutions. Except for a few tetraalkylammonium salts⁴, viscosity and density studies of 1:1 electrolytes in tetramethylurea (TMU) have not been reported. In continuation of our earlier studies in TMU^{5,6}, we report here the results of our studies on viscosities of some 1:1 electrolytes in TMU at 25°.

Tetramethylurea (Fluka AG) was purified as reported⁵ (b.p. = 76 -5°/12 mm, density = 0.9616 g cm⁻³, viscosity 1.404 × 10⁻² P and sp. cond. = 2.5 × 10⁻⁸ ohm⁻¹ cm⁻¹). The electrolytes used were prepared and/or purified by the methods already reported⁷.

Viscosities were measured with a modified Ubbelohde capillary type viscometer⁸ fitted with silica

gel guard tubes in an electrically controlled water thermostat (± 0.01°). Four to six measurements were made for each concentration. The viscometer was calibrated with carbon tetrachloride (BDH AR, b.p. = 78.2°; η = 9.019 × 10⁻³ P; d = 1.584 g cm⁻³) and freshly distilled benzene (BDH AR, m.p. = 5.51; η = 5.996 × 10⁻³ P; d = 0.8737 g cm⁻³).

Densities were determined using bicapillary pycnometer (capacity 9.5525 ml) which was calibrated with doubly distilled mercury (reproducibility ± 0.0001 g cm⁻³).

The viscosities of various solutions were calculated after applying kinetic energy correction⁸.

Densities and viscosities of alkali metal and ammonium perchlorates, sodium and potassium thiocyanates and lithium and tetrabutylammonium bromides have been measured in the concentration range 3.2 - 128.9 × 10⁻³ mole litre⁻¹ at 25° in tetramethylurea. The data have been analysed by the Jones-Dole equation⁹ (Eq. 1),

$$\eta/\eta_0 = 1 + AC^{1/2} + BC \quad \dots(1)$$

where η and η₀ are the viscosities of the solution and of pure solvent respectively and *A* and *B* are viscosity coefficients characteristic of the ions and the solvent. The viscosity *A* and *B* coefficients have been computed by least squares method from the plots of (η/η₀⁻¹)/C^{1/2} versus C^{1/2}. The results are recorded in Table 1. The *B* value for tetrabutylammonium bromide obtained here agrees quite satisfactorily with the value reported by Barker and Caruso⁴ (1.91 ± 0.05).

The viscosity *A* coefficients for NaSCN, RbClO₄ and NH₄ClO₄ have negative values. Although this has no physical meaning, similar observations have already been reported for tetraalkylammonium salts in TMU⁴ and for some 1:1 electrolytes in other non-aqueous solvents¹⁰⁻¹¹. This coefficient can also be calculated theoretically² from the limiting equivalent conductances and physical properties of the solvent. The values calculated for various electrolytes in TMU are also recorded in Table 1. However, theoretical *A* values for LiClO₄ and NH₄ClO₄ could not be calculated for the want of corresponding conductance data. The agreement between theoretical and experimental *A* values is satisfactory only in a few cases.

Table 1 shows that all the *B* values are positive

TABLE 1 — VALUES OF *A* AND *B*-COEFFICIENTS FOR SOME 1:1 ELECTROLYTES IN TMU AT 25°

| Electrolyte | <i>A</i> | | <i>B</i> |
|----------------------------------|----------|------------|----------|
| | (Expl) | (Theoret.) | (Expl) |
| LiBr | 0.0267 | 0.0203 | 1.83 |
| LiClO ₄ | 0.0318 | — | 1.57 |
| NaClO ₄ | 0.0561 | 0.0202 | 1.48 |
| Na SCN | -0.0065 | 0.0195 | 1.63 |
| KClO ₄ | 0.0727 | 0.0203 | 1.29 |
| KSCN | 0.0106 | 0.0185 | 1.35 |
| RbClO ₄ | -0.0051 | 0.0200 | 1.26 |
| CsClO ₄ | 0.0189 | 0.0197 | 1.09 |
| NH ₄ ClO ₄ | -0.0289 | — | 1.36 |

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showing thereby structure making⁹ effect of the ions in TMU. With the exception of ammonium perchlorate, *B* values of the electrolytes, having a common anion, decrease with increase in size of the cation. This may be attributed to the decreasing solvation with decreasing surface charge density as a result of which the size of primary solvation sheath decreases and consequently *B* values decrease with increasing size of the ion. This behaviour is in agreement with the results of conductance and thermochemical studies^{5,6,12}. However, the anomalous behaviour of NH_4^+ ion has been explained to be due to the ability of this tetrahedral ion to fit into the structure of the solvent with minimum steric disturbance. Consequently there is an increase in *B* value.

Thus, the present studies support the earlier studies^{5,6}, regarding the solvation behaviour of 1:1 electrolytes in TMU.

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Kinetics of Ion Exchange of a Negatively Charged Chloride Complex of Bismuth(III)

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The interdiffusion coefficients as well as the first order rate constants for $\text{BiCl}_5^{2-}/\text{Cl}^-$ exchange on Wofatit SBW resin (8% DVB) have been estimated statically. The observed values of $t_{1/2}$ have been evaluated under conditions favouring the particle diffusion mechanism. The energy of activation due to particle diffusion comes out to be 31.8 kJ mol⁻¹ compared with 26.4 kJ mol⁻¹ due to first order chemical reaction mechanism. The ion exchange process under study is found to be first order, controlled by the slow particle diffusion mechanism.

NEGATIVELY charged chloride complexes of Bi(III) in hydrochloric acid solutions have been

suggested¹ to be BiCl_4^- and BiCl_5^{2-} . A striking similarity of results of solvent extraction by ethers and anion exchange adsorbability indicated² that solvent extraction from chloride solutions might occur most readily if the extracted species has the composition MCl_4 . This conclusion supported the existence of the complex BiCl_5^{2-} in HCl solution since negligible solvent extraction was found for it^{1,3}. A decrease in adsorption of Bi(III) with increase in hydrochloric acid concentration (0.25 to 12 M HCl) has been reported^{1,4} on a strongly basic quaternary amine anion exchange resin.

In the literature there are some contributions^{5,6} which envisage the exchange velocity to be controlled by a chemical rate mechanism based on the law of mass action. Although it is possible that chemically controlled processes may occasionally govern ion exchange rates, an increasing weight of evidence^{7,8} favours the view that diffusion is the most common mechanism.

The purpose of the present investigation on the kinetics of $\text{BiCl}_5^{2-}/\text{Cl}^-$ exchange system is to test as to which of the mechanisms is applicable.

Strong base anion exchanger Wofatit SBW (8% DVB), described previously^{9,10} was used in the chloride form. The average diameter of the resin beads was 0.5 mm. The capacity of the exchanger was determined statically with the aid of the batch-method and found to be equal to 4 meq/g dry resin.

An appropriate quantity of BiCl_3 (AR) was dissolved in 1 M HCl (AR) and the solution was made up to 2 litres. The trivalent bismuth in the hydrochloric acid solution was determined volumetrically by titrating against EDTA in presence of xylenol orange as an indicator. At the end point the colour changed sharply from red to orange yellow¹¹. The concentration of the bismuth solution (referred to as Bi^{3+} -ions) was 400 mg/100 ml 1 N HCl, i.e., 57.42 meq/litre.

In order to restrict the anions present in the set of exchange experiments to BiCl_5^{2-} and Cl^- only, bismuth solution and the exchanger were taken in the chloride forms. The limited-bath technique^{12,13} was used to follow the concentration difference of bismuth during the ion exchange between BiCl_5^{2-} in the solution and Cl^- on the SBW resin. The measurements were carried out at various temperatures in the range 20° to 35°C maintained with an accuracy of $\pm 0.1^\circ\text{C}$. The amount of BiCl_5^{2-} exchanged on the resin was estimated from the concentration difference between the bismuth solutions before and after the ion exchange.

The rate-determining step in ion exchange⁸ is interdiffusion of the exchanging counter ions either within the ion exchanger itself (particle diffusion) or in an adherent liquid film which is not affected by agitating the solution (film diffusion).

The ion exchange system has been investigated under conditions favouring particle diffusion mechanism. The amount of BiCl_5^{2-} exchanged at different time intervals and at different temperatures is shown in Fig. 1. The fractional attainment of equilibrium, $U(t)$ is given by the ratio of the amount (Q_t), of