

On the Study of Triple Ion Formation

PER BERONIUS and TURE LINDBÄCK

Department of Physical Chemistry, University of Umeå, S-901 87 Umeå, Sweden

The formation of triple ions of lithium bromide in 1-octanol at 25 °C has been studied by electrical conductance measurements over the concentration range 0.42×10^{-4} to 42×10^{-4} M assuming equal probabilities of forming Li_2Br^+ and LiBr_2^- . The conductivity data at concentrations below 3.5×10^{-4} M, where triple ion formation was found to be negligible, which is in accord with theory, were employed to calculate the ion pair association constant (K_A) and the limiting conductivity of simple ions (Λ_∞). The triple ion association constant (K_T) and the limiting conductivity of ion triples (Λ_∞^T) were computed from a conductance equation involving these quantities as adjustable parameters. A mobility correction factor was incorporated in this equation to correct for ion atmosphere effects. Two different forms of this correction factor were investigated.

There exists a vast literature on ion pair formation in organic electrolyte systems as studied by means of electrical conductance measurements, *cf.* Refs. 1–5. A survey of the literature reveals, however, that comparatively few investigations of this kind concerning the formation of higher aggregates, such as triple ions, quadrupoles *etc.*, have been performed. There is an urgent need for further research in this field.

Previous investigations of triple ion formation are based on rather arbitrary assumptions concerning the limiting conductivity of these species. Ion atmosphere effects have not infrequently been neglected in the calculations. The objective of the present research is to investigate the formation of triple ions by means of electrical conductance measurements taking ion atmosphere effects into account. In this article, where conductance data for lithium bromide in 1-octanol at 25 °C are reported, a method for the derivation of both the triple ion association constant and the limiting conductivity of ion triples is outlined.

EXPERIMENTAL

Materials. The solvent (1-octanol, Fisher, *puriss*) was dried by shaking with Drierite (anhydrous calcium sulfate) for 24 h and fractionally distilled. The corrected⁶ density at 25 °C, determined by means of a Lipkin type pycnometer⁶ of 11 cm³ capacity, was $0.82172 \text{ g cm}^{-3}$ (*lit.*⁷ $0.82209 \text{ g cm}^{-3}$). The electrolytic conductivity was $1 \times 10^{-11} \Omega^{-1} \text{ cm}^{-1}$. The literature⁸ values, $\epsilon = 9.85$ for the relative permittivity, and $\eta = 0.073 \text{ P}$ for the viscosity, were used.

Lithium bromide (Merck, *suprapur*) was dried for 2 h at 200 °C.

Solutions were prepared by weight. The density, $0.82377 \text{ g cm}^{-3}$, of the most concentrated stock solution used (0.02623 M) was determined as above. A linear⁹ relationship between the density of the solution and the concentration of lithium bromide was assumed in the calculations.

Measurements. Conductivity measurements were performed at 25.00 ± 0.02 °C using a Leeds and Northrup 4666 conductivity bridge. The conductivity cell, which was fitted with bright platinum electrodes, was of the Daggett-Bair-Kraus type.¹⁰ The cell constant, determined by several calibrations using aqueous potassium chloride,¹¹ was 0.062026 cm^{-1} .

A portion of the pure solvent was transferred to the cell and its resistance established. Several 10 ml portions from a stock lithium bromide solution were then added by means of a syringe. The exact amount of each portion added was determined by differential weighing of the syringe. After each addition the cell resistance was established by measurements at different frequencies between 2 and 3.3 kHz and extrapolation to infinite frequency performed.

Because the resistances were in most instances outside the range of the conductivity bridge a 20 k Ω precision resistor was connected in parallel with the cell. For checking purposes a few measurements were performed using a 30 k Ω precision resistor.

Table 1. Conductance data for LiBr in 1-octanol at 25.0 °C.

$c \times 10^4$ M	Λ $\text{cm}^2 \Omega^{-1} \text{mol}^{-1}$	$c \times 10^4$ M	Λ $\text{cm}^2 \Omega^{-1} \text{mol}^{-1}$
0.42394	1.9040	7.2871	0.64228
0.44963	1.8649	7.6699	0.63148
0.85233	1.4983	8.0810	0.61588
0.90227	1.4667	8.4187	0.60814
1.2910	1.2853	8.8939	0.59244
1.3633	1.2565	9.1844	0.58715
1.7017	1.1557	9.6630	0.57270
1.7901	1.1318	11.818	0.53004
2.1024	1.0632	14.054	0.49496
2.2171	1.0383	16.284	0.46741
2.4953	0.99347	18.456	0.44535
2.6387	0.96949	20.620	0.42675
2.8915	0.93699	22.787	0.41098
3.0533	0.91425	24.635	0.39893
3.6810	0.85067	26.755	0.38686
3.9438	0.82424	28.785	0.37693
4.5339	0.78156	30.626	0.36817
4.8031	0.76075	32.548	0.36020
5.3342	0.73173	34.366	0.35315
5.6220	0.71363	36.251	0.34664
6.1154	0.69227	38.093	0.34061
6.4569	0.67449	39.914	0.33497
6.8852	0.65983	41.831	0.32954

Almost identical resistances of the cell were obtained for the two different shunt resistors used.

RESULTS AND DISCUSSION

The molar conductivity (Λ), corrected for the conductivity of the solvent, is given in Table 1 for several different concentrations, c , of lithium bromide.

Concentration range for ion pair formation. To determine the upper concentration limit for which triple ion formation is negligible the following procedure was used. The conductance equation,

$$\Lambda = \Lambda_{\infty} - Sc_i^{1/2} + Ec_i^{10} \log c_i + J_1 c_i - J_2 c_i^{3/2} - K_A c_i \alpha \gamma^2 \Lambda \quad (1)$$

where

$$\Lambda_{\infty} = \lambda_{\infty}(\text{Li}^+) + \lambda_{\infty}(\text{Br}^-) \quad (2)$$

and c_i is the concentration of free ions, was fitted to the seven lowest concentration points (c, Λ) to obtain the values of Λ_{∞} and K_A which minimize $\sigma(\Lambda)$, the

standard deviation between experimental and calculated Λ -values. This procedure was repeated upon increasing successively the upper limit of the concentration interval studied, *i.e.* eqn. (1) was fitted to the eight, nine, *etc.* lowest concentration points.

Two different forms of eqn. (1) were used, *viz.* the Pitts' equation¹² in the form of Fernández-Prini and Prue¹³ ("PFPP" equation) and the Fuoss-Hsia equation^{14,15} in the form of Fernández-Prini¹⁶ ("FHFP" equation).

The coefficients S and E in eqn. (1), which are of the same form in the PFPP and FHFP equations, respectively, are functions of Λ_{∞} , ϵ , η , and the temperature. The J -coefficients, which are of different forms for the two conductance equations concerned are, in addition, functions of R , the maximum center-to-center distance between the ions in the ion pair. The distance parameter, R , was set equal to the Bjerrum radius, *cf.* Refs. 17–19, which for octanol at 25 °C amounts to 28.45 Å for the charge type of electrolyte concerned.

The degree of dissociation, α , was calculated from the law of mass action for the equilibrium between free ions and ion pairs,

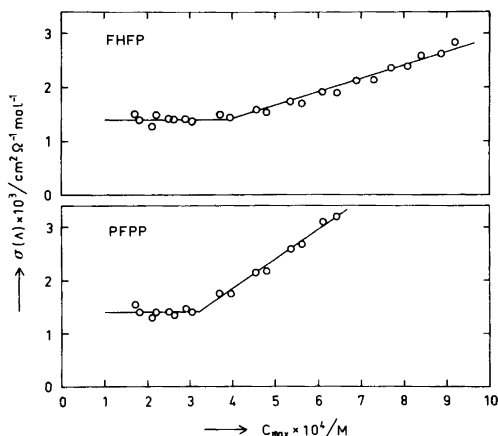


Fig. 1. Dependence of $\sigma(\Lambda)$ on maximum electrolyte concentration for application of the PFPP and FHFP versions of eqn. (1) to conductivity data of LiBr in 1-octanol at 25 °C.

$$K_A = (1 - \alpha)/(c\gamma^2\alpha^2) \quad (3)$$

where γ is the mean molar activity coefficient of free ions, which was calculated from the Debye-Hückel equation,

$$^{10}\log \gamma = -11.465c_i^{1/2}/(1 + 26.401c_i^{1/2}) \quad (4)$$

corresponding to the values of ϵ and R quoted above.

The computer program used to calculate Λ_∞ , K_A , and $\sigma(\Lambda)$ for a given value of R has been described.²⁰

Graphical representations of the dependence of $\sigma(\Lambda)$ on the maximum concentration of lithium bromide are shown in Fig. 1 for the two different forms of eqn. (1) discussed. For concentrations above approximately 3.5×10^{-4} M the fit of eqn. (1) to the experimental points gradually deteriorates as reflected by the increasing values of $\sigma(\Lambda)$. This is so for both the PFPP and FHFP versions of eqn. (1). The effect observed may be ascribed the formation of triple ions, *cf.* Ref. 21 and references therein.

For 1:1-electrolyte solutions at 25 °C Fuoss has derived the following relationship,⁵

$$c_{\max} = 3.2 \times 10^{-7} \epsilon^3 \quad (5)$$

between the maximum concentration, for which triple ion formation is negligible, and the permit-

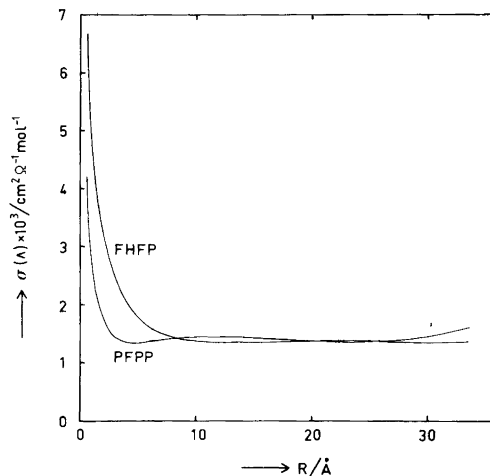


Fig. 2. Dependence of $\sigma(\Lambda)$ on distance parameter, R , for application of the PFPP and FHFP versions of eqn. (1) to conductivity data of LiBr ($c \leq 3.0533 \times 10^{-4}$ M) in 1-octanol at 25 °C.

tivity of the solvent. For the solvent studied eqn. (5) yields, $c_{\max} = 3.1 \times 10^{-4}$ M, which is in excellent agreement with the experimental value of 3.5×10^{-4} M arrived at above.

It is concluded that the 14 lowest concentration points in Table 1 may be used to compute the constants of eqn. (1). With $R = 28.45$ Å the following values were obtained. PFPP equation: $\Lambda_\infty = 3.9214$ cm² Ω⁻¹ mol⁻¹; $S = 41.07$; $E = 890.4$; $J_1 = 5610$; $J_2 = 123\,600$; $K_A = 56\,180$ (M⁻¹); FHFP equation: $\Lambda_\infty = 3.9479$; $S = 41.21$; $E = 897.5$; $J_1 = 5152$; $J_2 = 61\,100$; $K_A = 57\,100$.

It may be noted that $\sigma(\Lambda)$ is quite insensitive to the value of R within the 5–30 Å range, see Fig. 2.

Triple ion formation. In the interpretation of the conductivity data in the higher concentration range ($c \geq 3.681 \times 10^{-4}$ M; *cf.* Table 1) equal probabilities of forming the two different kinds of triple ions, Li_2Br^+ and LiBr_2^- , will be assumed.

The following equilibria will be considered.



The equilibrium constants of (IIa) and (IIb), being equal according to the assumption above, are denoted K_T . Putting,

$$[\text{Li}^+] = [\text{Br}^-] = c\alpha \quad (6)$$

$$[\text{Li}_2\text{Br}^+] = [\text{LiBr}_2^-] = c\alpha_T \quad (7)$$

we obtain eqn. (8) for the concentration of ion pairs.

$$[\text{LiBr}] = c(1 - \alpha - 3\alpha_T) \quad (8)$$

Hence,

$$K_A = (1 - \alpha - 3\alpha_T)/(c\gamma^2\alpha^2) \quad (9)$$

$$K_T = \alpha_T/[c\alpha(1 - \alpha - 3\alpha_T)] \quad (10)$$

The molar conductivity is given by the expression,

$$\Lambda = m(\alpha\Lambda_\infty + \alpha_T\Lambda_\infty^T) \quad (11)$$

where

$$\Lambda_\infty^T = \lambda_x(\text{Li}_2\text{Br}^+) + \lambda_x(\text{LiBr}_2^-) \quad (12)$$

and m is a mobility correction factor, which corrects Λ for ion atmosphere effects. This correction factor was calculated from the expression,

$$m = (\Lambda_\infty - S c_i^{1/2} + E c_i^{10} \log c_i + J_1 c_i - J_2 c_i^{3/2})/\Lambda_\infty \quad (13)$$

where the coefficients are the same as in eqn. (1) and,

$$c_i = c(\alpha + \alpha_T) \quad (14)$$

Eqn. (11) was fitted to the experimental conductivity data of the higher concentration range using a computer program operating as follows.

For each experimental point (c, Λ) a first approximation for α was calculated from eqn. (9) putting $\gamma = 1$ and $\alpha_T = 0$ using the K_A -value computed above from the conductivity data of the lower concentration range.

Using a preselected value of K_T a preliminary value of α_T was then obtained from eqn. (10).

A preliminary value for γ was calculated from the activity coefficient expression, eqn. (4), using c_i according to eqn. (14).

The new values of α_T and γ were inserted into eqn. (9) to obtain a better estimate of α , and so on.

These calculations were repeated until the difference between successive α -values, as well as between successive α_T -values, was less than 1×10^{-6} .

After attainment of the desired convergence in α and α_T the mobility correction term was calculated from eqn. (13) using the values of Λ_∞ , S , E , J_1 , and J_2 computed above.

Using a preselected value of Λ_∞^T eqn. (11) yielded a calculated Λ -value and, hence, the difference,

$$\Delta\Lambda = \Lambda(\text{exp}) - \Lambda(\text{calc}) \quad (15)$$

The expression,

$$\sigma(\Lambda) = \left(\frac{\sum(\Delta\Lambda)^2}{N-2} \right)^{1/2} \quad (16)$$

where N is the number of experimental points, was used to obtain the standard deviation between experimental and computed Λ -values.

To find the values of K_T and Λ_∞^T which minimize $\sigma(\Lambda)$ the dependence of $\sigma(\Lambda)$ on K_T was established for a series of values of the quotient, $\Lambda_\infty^T/\Lambda_\infty$. Since it seems improbable that the limiting conductivity of the triple ions would exceed that of the simple ions the calculations were restricted to values of $\Lambda_\infty^T/\Lambda_\infty \leq 1$.

Some results of these calculations are shown graphically in Fig. 3, which reveals that well-defined minima are obtained.

In Fig. 4 the conditional minimum $\sigma(\Lambda)$ has been plotted vs. the ratio, $\Lambda_\infty^T/\Lambda_\infty$. The corresponding

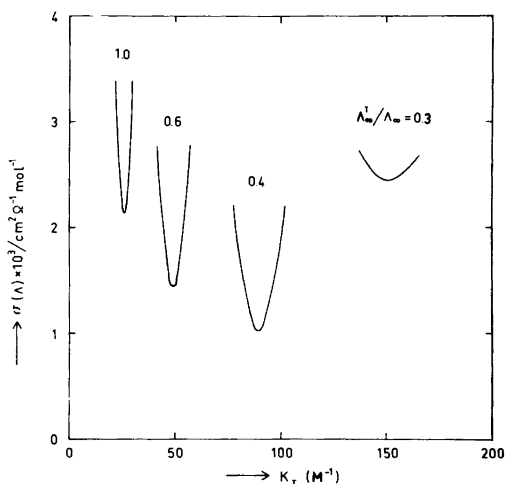


Fig. 3. Dependence of $\sigma(\Lambda)$ on K_T and the ratio, $\Lambda_\infty^T/\Lambda_\infty$, for application of the F version of eqn. (11) to conductivity data of LiBr ($c \geq 3.681 \times 10^{-4}$ M) in 1-octanol at 25 °C.

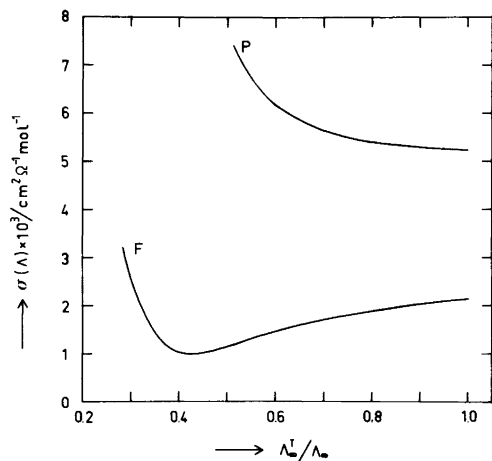


Fig. 4. Dependence of conditional minimum $\sigma(\Lambda)$ on the ratio, $\Lambda_\infty^T/\Lambda_\infty$, for application of the P and F versions of eqn. (11) to conductivity data for LiBr ($c \geq 3.681 \times 10^{-4}$ M) in 1-octanol at 25 °C.

graph of the dependence of K_T on this ratio is shown in Fig. 5. The curves labelled "P" and "F" in Figs. 4 and 5 were obtained using the two different versions of eqn. (11) based on the conductance parameter values quoted above for the PFPP and FHFP equations, respectively. According to the curves in Fig. 4 the F version of eqn. (11) results in the better fit to the experimental points.

By contrast with the P curve in Fig. 4 the F curve exhibits a minimum, which appears at a limiting conductivity of the triple ions corresponding to $\Lambda_\infty^T \approx 0.4\Lambda_\infty$. This observation suggests that the limiting conductivity of the triple ions is about half that of the single ions. Compare previous studies in which the limiting conductivity of the

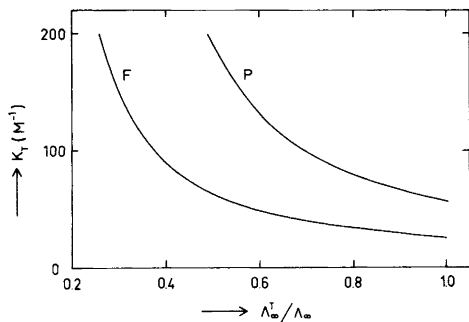


Fig. 5. Dependence of K_T on the ratio, $\Lambda_\infty^T/\Lambda_\infty$, for LiBr in 1-octanol at 25 °C.

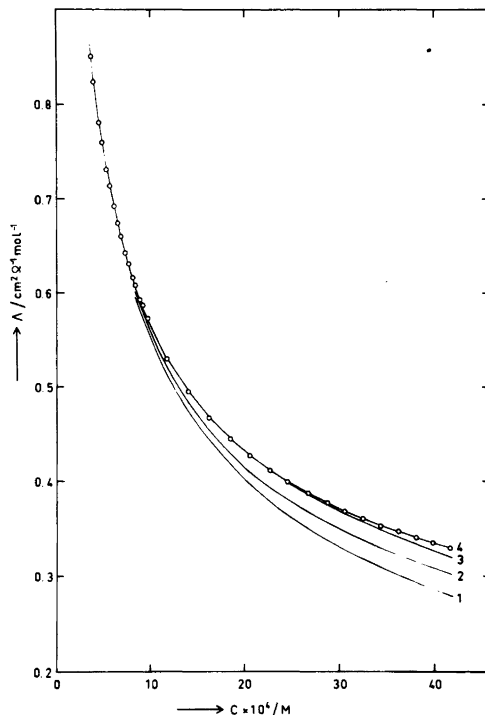


Fig. 6. Experimental and calculated values of Λ vs. concentration of LiBr in 1-octanol at 25 °C. Curves 1 and 2: PFPP and FHFP versions, respectively, of eqn. (1). Curves 3 and 4: P and F versions, respectively, of eqn. (11).

triple ions has been assumed equal to 1/3 of that of the simple ions in some investigations, *e.g.* in Ref. 21, and equal to 2/3 in others, see for instance Ref. 22.

The experimental points (c, Λ) of the higher concentration range are shown graphically, together with calculated curves, in Fig. 6. Curve 1 is an extrapolation of the PFPP version of eqn. (1) from the lower to the higher concentration range, while curve 2 is the corresponding extrapolation of the FHFP version of eqn. (1). Curve 3 represents the P version of eqn. (11) for $\Lambda_\infty^T/\Lambda_\infty = 1$ and $K_T = 57$ referring to the minimum value of $\sigma(\Lambda)$ of curve P in Fig. 4. Curve 4 is the corresponding representation of the F version of eqn. (11) referring to the minimum of curve F in Fig. 4 for $\Lambda_\infty^T/\Lambda_\infty = 0.43$ and $K_T = 80$. As may be seen from Fig. 6 an excellent fit of eqn. (11) to the experimental points of the higher concentration range is obtained in this latter case.

As mentioned above previous investigations are based on rather arbitrary assumptions concerning the limiting conductivity of the triple ions. According to the present study the minimum value of $\sigma(\Lambda)$ corresponds to a limiting conductivity of the triple ions, which is about half that of the single ions. It is a matter for further research to verify whether the location of this minimum, *cf.* Fig. 4, indeed reflects the true value of the limiting conductivity of the triple ions.

The present formalism used to analyze conductance data assuming ion pair and triple ion formation necessarily involves a great number of adjustable parameters. Furthermore, the numerical value of the triple ion association constant may be rather strongly dependent on basic assumptions made, *e.g.* concerning ion atmosphere effects, *cf.* Fig. 5. Consequently, it seems worthwhile to stress that the calculated value of K_T should be used with caution.

Acknowledgements. The authors thank Mrs. Margareta Ögren for technical assistance and the Swedish Natural Science Research Council for financial support.

REFERENCES

- Gordon, J. E. *The Organic Chemistry of Electrolyte Solutions*, Wiley, New York 1975.
- Covington, A. K. and Dickinson, T., Eds., *Physical Chemistry of Organic Solvent Systems*, Plenum, London 1973.
- Janz, G. J. and Tomkins, R. P. T. *Nonaqueous Electrolytes Handbook*, Academic, New York 1972, Vol. 1.
- Conway, B. E. and Barradas, R. G., Eds., *Chemical Physics of Ionic Solutions*, Wiley, New York 1966.
- Fuoss, R. M. and Accascina, F. *Electrolytic Conductance*, Interscience, New York 1959.
- Bauer, N. and Lewin, S. Z. In Weissberger, A., Ed., *Physical Methods of Organic Chemistry*, 3rd Ed., Interscience, New York 1959, Vol. I, Part I, Chapter IV.
- Weissberger, A., Ed., *Technique of Chemistry, Organic Solvents*, 3rd Ed., Wiley-Interscience, New York 1970, Vol. II, p. 181.
- Shkodin, A. M., Sadovnichaya, L. P. and Podolyanko, V. A. *Ukr. Khim. Zh.* 35 (1969) 144.
- Nilsson, A.-M. and Beronius, P. *Z. Phys. Chem. (Frankfurt am Main)* 79 (1972) 83.
- Daggett, Jr., H. M., Bair, E. J. and Kraus, C. A. *J. Am. Chem. Soc.* 73 (1951) 799.
- Lind, Jr., J. E., Zwolenik, J. J. and Fuoss, R. M. *J. Am. Chem. Soc.* 81 (1959) 1557.
- Pitts, E. *Proc. R. Soc. London A* 217 (1953) 43.
- Fernández-Prini, R. and Prue, J. E. *Z. Phys. Chem. (Leipzig)* 228 (1965) 373.
- Fuoss, R. M. and Hsia, K.-L. *Proc. Natl. Acad. Sci. U.S.A.* 57 (1967) 1550.
- Fuoss, R. M. and Hsia, K.-L. *Proc. Natl. Acad. Sci. U.S.A.* 58 (1968) 1818.
- Fernández-Prini, R. *Trans. Faraday Soc.* 65 (1969) 3311.
- Justice, J.-C. *Electrochim. Acta* 16 (1971) 701.
- Beronius, P. *Acta Chem. Scand. A* 29 (1975) 289.
- Beronius, P. *Acta Chem. Scand. A* 30 (1976) 115.
- Beronius, P. *Acta Chem. Scand. A* 28 (1974) 77.
- Robinson, R. A. and Stokes, R. H. *Electrolyte Solutions*, Butterworths, London 1965, Chapter 14.
- Ralph, E. K. and Gilkerson, W. R. *J. Am. Chem. Soc.* 86 (1964) 4783.

Received December 27, 1977.