

Properties of Sodium Iodide in 1-Octanol at 25 °C. A Conductimetric Study

PER BERONIUS

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

Comprehensive information regarding various interactions in electrolyte solutions may be provided by the very precise conductimetric method. In connection with investigations of solvent effects on the character of ion pairs, which may consist of ions in contact or of pair of ions separated by solvent molecules,¹ conductance measurements of highly diluted solutions of sodium iodide in 1-octanol at 25 °C were undertaken. The objective of this communication is to report the results and a few conclusions. This system has been studied previously by Shkodin *et al.*² but their data are of insufficient precision for our purposes.

Experimental. The electrolyte (sodium iodide, Merck, *suprapur*) was predried for 2 h at 110 °C and again dried under these conditions immediately before use. Precautions were taken to avoid absorption of moisture from the air. The solvent (1-octanol, Riedel De Haen AG), containing less than 0.018 vol. % of water according to Karl Fisher titration, was flushed for 3 h with dry nitrogen to remove dissolved oxygen; electrolytic conductivity, $\kappa = 2.9 \times 10^{-9}$ (Run A) and 3.8×10^{-9} S cm⁻¹ (Run B).

The equipment used and the method of performing the conductivity measurements have been described.³

Table 1. Experimental data for NaI in 1-octanol at 25 °C.

Run A $c \times 10^4$ M	Λ S cm ² mol ⁻¹	Run B $c \times 10^4$ M	Λ S cm ² mol ⁻¹
0.62619	2.1529	0.54937	2.2333
0.83114	1.9624	1.0937	1.7793
1.0342	1.8192	1.6331	1.5412
1.2355	1.7096	2.1676	1.3868
1.4350	1.6203	2.6973	1.2769
1.6327	1.5450		
1.8287	1.4810		
2.0229	1.4255		
2.2154	1.3774		
2.4062	1.3347		
2.5954	1.2967		
2.7830	1.2625		
2.9689	1.2312		

Results and conclusions. Conductance data for two different runs are given in Table 1, where the molar conductivity, Λ , is quoted for several different sodium iodide concentrations in the interval, $5 \times 10^{-5} < c < 3 \times 10^{-4}$ M. The measurements must necessarily be confined to this narrow concentration interval because of disturbing triple ion formation at higher concentrations⁴ and deteriorating precision at lower concentrations.

The ion pair association constant, K_A , and the limiting molar conductivity, Λ_∞ , were calculated from the recent conductance equation of Fuoss,⁵ which for pairwise associated symmetrical electrolytes may be written,

$$\Lambda = \Lambda_\infty(1 - \Delta X/X) - \Delta\Lambda_e - K_A \alpha \gamma^2 \Lambda \quad (1)$$

where $\Delta X/X$ is the relaxation term, $\Delta\Lambda_e$ is the electrophoretic term, α is the unassociated fraction of the electrolyte, and γ is the mean activity coefficient of free ions, which was calculated from the Debye-Hückel equation in the form used in Ref. 6. The distance parameter in eqn. (1) and in the Debye-Hückel equation was set equal to the Bjerrum radius, which for univalent electrolytes in 1-octanol at 25 °C (relative permittivity,² $\epsilon = 9.85$) amounts to 28.45 Å. The value, $\eta = 0.073$ P, for the viscosity² of the solvent was used. The computer programme used for these calculations is similar to that outlined in Ref. 6.

The values of K_A and Λ_∞ computed are given together with their standard deviations in Table 2, where $\sigma(\Lambda)$ is the standard deviation⁶ between measured and calculated Λ values.

A graph according to eqn. (1), rewritten in linear form, is shown in Fig. 1. It is evident from this graph that the evaluation of Λ_∞ implies a quite long extrapolation. In spite of this Λ_∞ was obtained with a relative standard deviation of only a few tenth's percent, cf. Table 2.

Table 2. Conductance parameters for NaI in 1-octanol at 25 °C.

Run	$K_A \times 10^{-2}$ M ⁻¹	Λ_∞ S cm ² mol ⁻¹	$\sigma(\Lambda)$ S cm ² mol ⁻¹
A	364 ± 1	4.389 ± 0.008	0.0007
B	353 ± 2	4.327 ± 0.016	0.0013
A + B	357 ± 2	4.353 ± 0.018	0.0025

Table 3. Data corresponding to eqn. (1) for 1-octanol as solvent at 25 °C.

Salt	$K_A \times 10^{-2}$ M ⁻¹	Λ_∞ S cm ² mol ⁻¹
NaI	357	4.35
LiBr	518	3.85

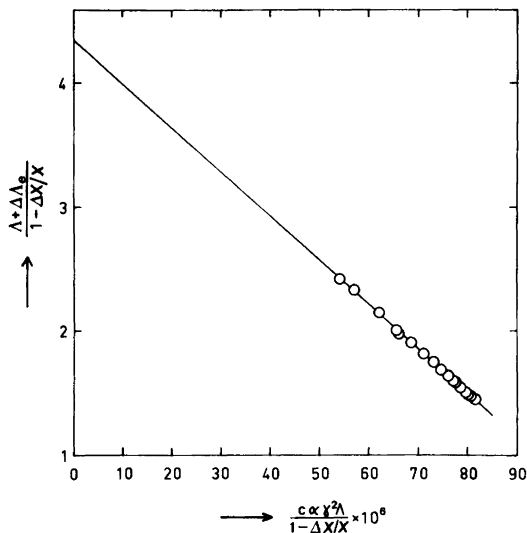


Fig. 1. Graph corresponding to eqn. (1) for NaI in 1-octanol at 25 °C.

Data according to eqn. (1) for lithium bromide³ and sodium iodide in 1-octanol are compared in Table 3. It is found that $K_A(\text{LiBr}) > K_A(\text{NaI})$. This finding indicates that lithium bromide forms more tight ion pairs than does sodium iodide. The fact that $\Lambda_{\infty}(\text{LiBr}) < \Lambda_{\infty}(\text{NaI})$ reflects stronger ion-solvent interactions for Li^+ and Br^- as compared with Na^+ and I^- , respectively. In view of the different surface charge densities of the naked ions this is what might be expected.

Limiting molar conductivities of the iodide ion, $\lambda_{\infty}(\text{I}^-)$, in methanol, ethanol, 1-propanol, and 1-butanol at 25 °C have been previously established^{7,8} (Table 4). The limiting transport number⁹ of the iodide ion, $t_{\infty}(\text{NaI})$, in these alcohols varies but slightly, viz. from 0.567 to 0.580. The value of $\lambda_{\infty}(\text{I}^-)$ referring to 1-octanol in Table 4 was calculated assuming $t_{\infty}(\text{NaI}) = 0.57$ in this solvent.

The conductivity and viscosity data in Table 4 were used to calculate the Stokes' radius of the iodide ion from the expression,¹⁰

Table 4. Data referring to n-alcohols at 25 °C.

Solvent	$\lambda_{\infty}(\text{I}^-)$ S cm ² mol ⁻¹	Ref.	η P	Ref.
MeOH	63.12	7	0.005445	11
EtOH	27.36	7	0.01078	11
PrOH	13.87	7	0.01952	12
BuOH	9.66	8	0.0246	13
OctOH	2.48	This work	0.073	2

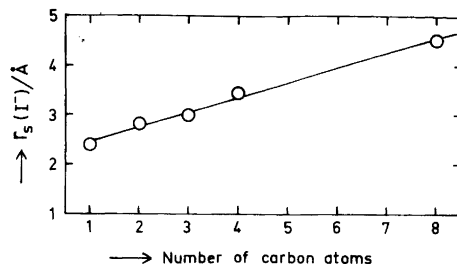


Fig. 2. Stokes' radius of the iodide ion in n-alcohols at 25 °C as a function of the number of carbon atoms in the solvent molecule.

$$r_s(\text{I}^-) = |z|F^2 / (6\pi N \eta \lambda_{\infty}) \quad (2)$$

where z is the valency of the ion, F is the Faraday constant, and N is the Avogadro constant. The results, shown in graphical form in Fig. 2, indicate that $r_s(\text{I}^-)$ increases linearly with the number of carbon atoms in the solvent molecule.

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- Winstein, S., Clippinger, E., Fainberg, A. H. and Robinson, G. C. *J. Am. Chem. Soc.* 76 (1954) 2597.
- Shkodin, A. M., Sadovnichaya, L. P. and Podolyanko, V. A. *Ukr. Khim. Zh.* 35 (1969) 144.
- Berionius, P. and Lindbäck, T. *Acta Chem. Scand. A* 32 (1978) 423.
- Fuoss, R. M. and Accascina, F. *Electrolytic Conductance*, Interscience, New York 1959, Chapter 18.
- Fuoss, R. M. *J. Phys. Chem.* 79 (1975) 525 and 1983.
- Berionius, P. *Acta Chem. Scand. A* 28 (1974) 77.
- Berionius, P. *Unpublished*.
- Vehlow, J. and Marx, G. *Naturwissenschaften* 58 (1971) 320.
- Ström, E. S. and Berionius, P. *Radiochem. Radioanal. Lett.* 18 (1974) 143.
- Robinson, R. A. and Stokes, R. H. *Electrolyte Solutions*, Butterworths, London 1965, p. 43.
- Riddik, J. A. and Bunger, W. B. *Techniques of Chemistry, Organic Solvents*, 3rd Ed., Wiley-Interscience, New York 1970, Vol. II.
- Evans, D. F. and Gardam, P. *J. Phys. Chem.* 72 (1968) 3281.
- Janz, G. J. and Tomkins, R. P. T. *Nonaqueous Electrolytes Handbook*, Academic, New York 1972, Vol. I.

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