

Aromatic Nucleophilic Exchange Reactions. Part II.¹ Solvent Effects

By D. F. Maundrell, C. H. Bovington, and B. Dacre,* Chemistry Department, Rutherford Laboratories, Royal Military College of Science, Shrivenham, Swindon, Wilts

Homogeneous and heterogeneous rates for exchange of iodine between ammonium iodide and 1-iodo-2,4-dinitrobenzene have been measured in a series of aliphatic alcohols as solvents. The homogeneous exchange can be understood in terms of the Laidler-Eyring theory of solvent effects. For the heterogeneous exchange, changes in the activity coefficient of the iodide ion may be the principal contributor to the observed solvent effect.

In Part I¹ we confirmed the second-order nature of the iodine exchange between potassium iodide and 1-iodo-2,4-dinitrobenzene in methanol and in addition observed a heterogeneous process which became the dominant exchange mechanism at low iodide-ion concentration. Here we report further work on the homogeneous exchange in four aliphatic alcohols. Application of the Laidler-Eyring theory to our results gives a reasonable value for the radius of the activated complex. Heterogeneous exchange at the solution-reaction flask interface is again seen to be important at low alkali-iodide concentrations.

EXPERIMENTAL

Materials.—Potassium iodide, 1-iodo-2,4-dinitrobenzene, and methanol were obtained and purified as already described.¹ AnalaR materials, ammonium iodide, ethanol, n-propanol, and n-butanol were further purified by the methods of Venkatesetty and Brown.²

Method.—The method was that described in Part I, except that the ratio-tracer was usually ¹²⁵I (Amersham Code IMSIP) added as iodide. This isotope (half-life 60.0 days) had obvious advantages compared with ¹³¹I (half-life 8.07 days) when individual experiments extended over a period of weeks. The 100-ml Pyrex reaction flasks were cleaned by steaming them for 1 h, rinsing them with AnalaR acetone, and finally drying them in a vacuum oven. Experiments were made, as in Part I, to check for solvolysis of iodide ion and 1-iodo-2,4-dinitrobenzene. We found no evidence for such reactions after a period of 7 days at 80 °C.

Counting Assembly.—A Packard Tri-Carb 2000 series liquid scintillation counter was used in the majority of experiments. ¹²⁵I Was counted with lower and upper discriminators set respectively at 100 and infinity at a gain of 45%. The liquid scintillator solution was a PPO-POPOP toluene mixture and weighed samples of 1-iodo-2,4-dinitrobenzene were added to 20 ml of this solution for counting. A quench calibration curve was prepared by measurement of the effect of inactive 1-iodo-2,4-dinitrobenzene on the counting rate of a standard ¹²⁵I sample. Corrections for quenching and radioactive decay were applied when necessary.

RESULTS AND DISCUSSION

Since exchange rates are first order with respect to 1-iodo-2,4-dinitrobenzene in the concentration ranges studied, data are presented primarily as first-order rate constants in this reactant. Table 1 lists the data for iodine exchange with ammonium iodide in n-butanol at 45 °C. Results on the exchange in methanol, ethanol,

and n-propanol are given in Table 2. A few results obtained for KI in n-butanol are also listed in Table 3 but work with this salt is limited by low solubility.

TABLE 1

First-order specific rate constants at 45 °C in n-butanol (*a* denotes the stoichiometric concentration of ammonium iodide and *b* that of 1-iodo-2,4-dinitrobenzene in the reaction mixture)

10 ⁴ <i>a</i> /M	10 ² <i>b</i> /M	10 ⁷ <i>k</i> ₁ /s ⁻¹	10 ⁴ <i>a</i> /M	10 ² <i>b</i> /M	10 ⁷ <i>k</i> ₁ /s ⁻¹
1952	1.124	4.43	1.26	2.494	4.4
997.5	2.435	2.32	1.08	1.218	1.64
976.1	1.213	2.21	0.976	1.220	1.89
480.5	1.218	1.08	0.908	2.490	4.2
107.7	1.216	0.347	0.800	2.150	1.6
48.80	1.274	0.266	0.800	2.567	4.1
48.05	1.218	0.280	0.699	2.494	3.6
10.77	1.222	0.376	0.600	2.490	7.2
9.76	1.220	0.324	0.538	4.878	3.5
4.81	1.216	0.502	0.538	2.305	4.1
4.81	1.218	0.576	0.538	1.218	2.4
			0.500	2.49	3.2

TABLE 2

Second-order specific rate constants at 45 °C (*a* denotes the stoichiometric concentration of ammonium iodide and *b* that of 1-iodo-2,4-dinitrobenzene)

Solvent	10 ³ <i>a</i> /M	10 ² <i>b</i> /M	10 ⁶ <i>k</i> ₂ (obs) l mol ⁻¹ s ⁻¹	α	10 ⁶ <i>k</i> ₂ l mol ⁻¹ s ⁻¹	ε
Methanol	100	2.5	0.59 ±0.02*	1.0	0.59	28.3 ^a
Ethanol	100	2.4	1.29 ±0.09*	0.64	2.02	21.0 ^a
n-Propanol	100	2.4	2.40 ±0.12*	0.57	4.21	17.9 ^b
n-Butanol	99.75	2.435	2.32	0.45	5.4	14.6 ^b
	97.61	1.213	2.27	0.45	5.0	
	48.05	1.218	2.24 †	0.45	5.2	
	10.77	1.216	3.05 †	0.48	6.4	
	4.880	1.274	4.59 †	0.55	8.3	
	4.805	1.218	4.93 †	0.55	9.0	

* Standard deviation in the mean of six experiments.

† These are the observed second-order rate constants corrected for the heterogeneous contribution which is approximately 14%.

^a H. Fellner-Feldegg, *J. Phys. Chem.*, 1969, **73**, 617.

^b S. K. Garg and C. P. Smyth, *J. Phys. Chem.*, 1965, **69**, 1294.

General.—For ammonium iodide concentrations greater than 0.1M the exchange is first order in the salt, *i.e.* overall second order. In this respect the exchange is similar to that between KI and 1-iodo-2,4-dinitrobenzene in methanol.¹ No experiments were done to establish overall second-order kinetics for the exchange in ethanol and n-propanol at high salt concentrations, *ca.* 0.1M, but

¹ Part I, C. H. Bovington, D. F. Maundrell, and B. Dacre, *J. Chem. Soc. (B)*, 1971, 767.

² H. V. Venkatesetty and G. H. Brown, *J. Phys. Chem.*, 1962, 2075.

there is no reason to expect different behaviour in these solvents.

On the assumption that exchange occurs only *via* free iodide ions and that direct exchange involving ion pairs

TABLE 3

First-order specific rate constants at 45 °C in n-butanol (*a* denotes the stoichiometric concentration of potassium iodide and *b* that of 1-iodo-2,4-dinitrobenzene in the reaction mixture)

$10^4 a/M$	$10^2 b/M$	$10^7 k_1/s^{-1}$	$10^4 a/M$	$10^2 b/M$	$10^7 k_1/s^{-1}$
43.54	2.501	0.280	0.316	2.665	6.9
5.24	1.186	0.55	0.1562	2.485	8.7
1.562	2.302	2.6	0.1562	2.221	5.3
1.260	2.374	2.0	0.126	2.488	5.8
1.260	2.374	2.0	0.100	2.667	5.6
0.524	1.258	3.2	0.100	2.837	2.4

is unimportant³ then comparison of results between solvents should be on the basis of free ion concentrations. At high salt concentrations we observe:

$$R = k_{2(\text{obs})} [24 \text{ DNIB}] [\text{NH}_4\text{I}]_{\text{stoich}} \quad (\text{i})$$

Where *R* is the rate of exchange

$$\text{We write } R = k_2 [24 \text{ DNIB}] [\text{I}^-] \quad (\text{ii})$$

Where $k_2 = k_{2(\text{obs})}/\alpha$ and α is the degree of dissociation (iii)

Calculation of α requires a knowledge of the dissociation constant and ion activity coefficient. Details of such calculations are given in an Appendix and the resulting values listed in column 5, Table 2. The first-order rate constants listed in Table 1 are plotted in Figure 1.

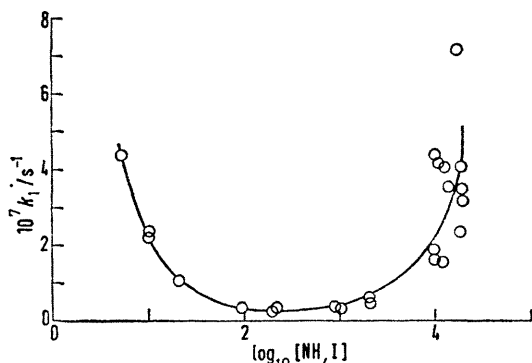


FIGURE 1 Ammonium iodide in n-butanol at 45 °C

There is a general similarity between this curve and that for potassium iodide 1-iodo-2,4-dinitrobenzene exchange in methanol; both homogeneous and heterogeneous mechanisms are again operating. Reproducibility of rate constants is however fairly poor in the n-butanol solutions for salt concentration $<10^{-4}\text{M}$. Initially we suspected the presence of varying amounts of important

³ P. Beronius, *Acta Chem. Scand.*, 1969, **23**, 3120.

⁴ A. J. Parker, *Chem. Rev.*, 1969, **69**, 1, for extensive references to previous work.

⁵ E. S. Amis, 'Solvent Effects on Reaction Rates and Mechanisms,' Academic Press, London, 1966, ch. 2.

impurities in the different batches of n-butanol used, but repeated low-pressure distillation of the solvent failed to improve the overall reproducibility of results. For convenience we shall discuss homogeneous and heterogeneous exchange separately.

Homogeneous Exchange.—Alkali-metal iodide concentration greater than 10^{-2}M . Considerable attention has been paid, recently, to the effects of solvents on ion-dipole reactions, particularly with regard to the often

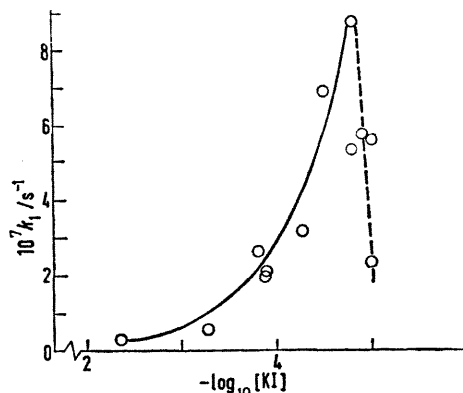


FIGURE 2 Potassium iodide in n-butanol at 45 °C

spectacular increase in rate constants which are observed on transfer from a protic solvent, *e.g.* methanol, to a dipolar aprotic solvent, *e.g.* dimethylformamide.⁴ The theories which have been developed for the effect of solvent on ion-dipole reactions generally predict a linear relationship between $\log k_2$ and $1/\epsilon$.⁵ Such relations fail completely when protic and dipolar aprotic solvent effects are compared.⁴ This failure is principally due to neglect of specific interaction between reactants and solvent molecules. An alternative approach, which seeks to interpret solvent effects in terms of changes in the activity coefficients of reactants and activated complex has been described and used by Parker.⁴ Little attention appears to have been given to the effect of a series of closely related solvents in which reactant-solvent interactions are approximately constant. Such conditions are probably satisfied for the series of alcohols studied in this work, so that the simpler theories may apply. The principal theories are due to Laidler and Eyring,⁶ Amis and Jaffé,⁷ and Laidler and Landskroener⁸ and have been reviewed by Amis. For an anion-dipole reaction the Laidler-Eyring equation predicts that an increase in dielectric constant should be accompanied by a decrease in the rate constant, whereas the Amis-Jaffé equation predicts the opposite effect. The Laidler-Landskroener theory allows for both effects but application is difficult since a detailed model of the activated complex is required.

For the alcohols methanol to n-butanol a plot of $\log k_2$

⁶ K. J. Laidler and H. Eyring, *Ann. N.Y. Acad. Sci.*, 1940, **39**, 303.

⁷ E. S. Amis and G. Jaffé, *J. Chem. Phys.*, 1942, **10**, 598.

⁸ K. J. Laidler and P. A. Landskroener, *Trans. Faraday Soc.*, 1956, **52**, 200.

against $1/\epsilon$ (Figure 3) has a mean value of the gradient of +36. For reasons evident from the foregoing paragraph

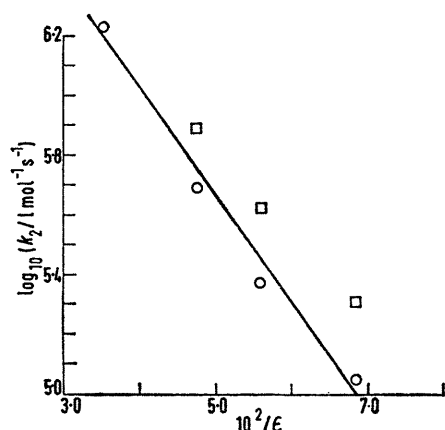


FIGURE 3 Dependence of rate constant on solvents
 $\square = \log(k_{2\text{obs}})$ against $1/\epsilon$, and $\circ = \log(k_{2\text{obs}}/a)$ against $1/\epsilon$

we have chosen to examine our results in terms of the Laidler-Eyring equation, viz:

$$\begin{aligned} \ln k_2 &= \ln k_0 + \frac{Z_{I-}^2 e^2}{2kT} \left(\frac{1}{\epsilon} - 1 \right) \left(\frac{1}{r_{I-}} - \frac{1}{r_{I^+}} \right) \\ &- \frac{Z_{I-}^2 e^2}{2kT \epsilon} \left[\frac{\kappa}{(1 + a_{I-} - \kappa)} - \frac{\kappa}{(1 + a_{I^+} \kappa)} \right] \\ &- \frac{1}{kT} \left(\frac{\epsilon - 1}{2\epsilon + 1} \right) \frac{\mu_D}{\alpha_D^2} + \left(b_D - b_{I^+} + \frac{\bar{\alpha} e^2}{\epsilon r kT} \right) I \\ &+ \left(\frac{\phi_{I-} + \phi_D - \phi_{I^+}}{kT} \right) \end{aligned} \quad (\text{iv})$$

where ϵ is the dielectric constant of the solvent, I is the ionic strength and μ_D the dipole moment of the organic iodide. All other symbols have the meanings ascribed in ref. 5.

We now examine the relative importance of terms which are influenced by the dielectric constant. At 45 °C the ratio $\frac{\epsilon - 1}{2\epsilon + 1}$ in term (4) is 0.47 and 0.45 for methanol and n-butanol respectively and hence is quite insensitive to changes in dielectric constant for the present series of solvents. According to Laidler and Eyring⁶ the contribution from term (5) is small due to cancellation of the Hückel and Debye-McAulay terms, and term (6) is also not sensibly influenced by the dielectric constant. A plot of $\log_{10} k_2$ against $1/\epsilon$ should therefore have a gradient of:

$$\frac{Z_{I-}^2 e^2}{2.303 \times 2kT} \left[\left(\frac{r_{I^+} - r_{I-}}{r_{I^+} \times r_{I-}} \right) - \frac{(a_{I^+} - a_{I-}) \kappa^2}{(1 + a_{I-} - \kappa)(1 + a_{I^+} \kappa)} \right] \quad (\text{v})$$

We can estimate the importance of the bracketed terms by taking reasonable values for a_{I-} and a_{I^+} and comparing the observed gradient with the κ^* term. We must evaluate the latter term for the conditions pertaining to the kinetic data, i.e. stoichiometric concentrations $\sim 0.1\text{M}$ in all solvents, i.e. ionic strength ca. 0.1 in methanol and ca. 0.02₆ in n-butanol. Taking $a_{I-} = 2 \times 10^{-8}$, $a_{I^+} = 4 \times 10^{-8}$ cm then with the appropriate ionic strengths we calculate a value of ca. 2.5×10^6 and ca. 1.5×10^6 for the κ term for methanol and butanol respectively. If instead we put $a_{I^+} = 6 \times 10^{-8}$ the corresponding figures are 4.2×10^6 and 2.6×10^6 . Since $a_{I^+} = 6 \times 10^{-8}$ is probably too large, the κ term seems unlikely to exceed 4.2×10^6 which would contribute ca. 4.9 to the gradient of the $\log_{10} k_2 - 1/\epsilon$ plot. This is only about 14% of the observed gradient of +36. Neglecting any corrections the quantity r_{I^+} is then calculated to be 10.0×10^{-8} cm, which is quite acceptable in view of the approximations made, and the theory gives an adequate interpretation of the observed solvent effect.

Heterogeneous Exchange in n-Butanol.—Alkali-metal iodide concentration less than 10^{-2}M . The first-order rate constant decreases as the stoichiometric concentration of ammonium iodide is reduced, and passed through minimum which occurs between 10^{-2} and 10^{-3}M as shown in Figure 1. Below 10^{-3}M a heterogeneous mechanism controls the exchange. Similar behaviour is seen when potassium iodide is substituted for ammonium iodide, but

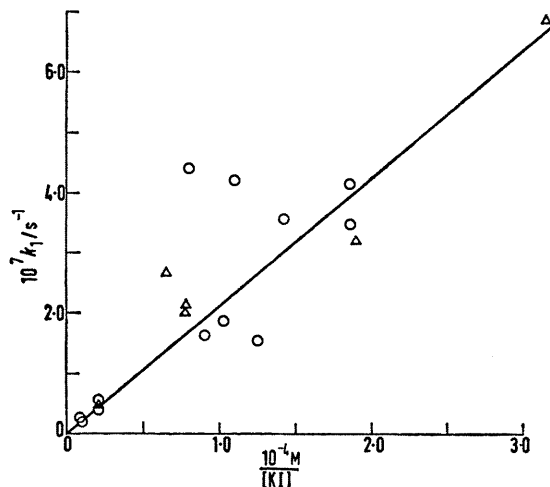


FIGURE 4 Inverse first-order relation $\circ = \text{NH}_4\text{I}$, $\Delta = \text{KI}$.
 Note: For the points at $10^{-4}\text{M}/[\text{KI}] = 0.1$ and 0.2 , the homogeneous contribution has been subtracted. Slope = 21.2×10^{-12}

for the former high concentration data ($>10^{-2}\text{M}$) are lacking due to low solubility in this solvent. Although results with each salt are rather scattered for concentrations less than 10^{-4}M there is evidence for a maximum in the curve which probably occurs at ca. 10^{-5}M for both

$$* \kappa = \left(\frac{4\pi e^2}{\epsilon kT} \sum_i n_i Z_i^2 \right)^{\frac{1}{2}}$$

salts. An equation of the Langmuir-Hinshelwood type *viz.* $k_1 = \frac{A[MI]}{(I + B[MI])^2}$ as used previously¹ would no doubt represent the general features of the curve, but because of scatter in the experimental points and the consequent uncertainty in derived constants, no attempt was made to fit the equation to our data. However, from the data at concentrations in the range $5 \times 10^{-5}M$ to $5 \times 10^{-4}M$ iodide ion, which appears to correspond with the region in which k_1 varies inversely as $[I^-]$ shown in Figure 4, we are able to calculate an approximate value for the quantity A/B^2 .¹ It is easily shown that

$$A/B^2 = k_2 K_2 / K_3 \quad (\text{vi})$$

where k_2 is the surface bimolecular rate constant and K_2 and K_3 are the adsorption equilibrium constants for 1-iodo-2,4-dinitrobenzene and iodide ion respectively. The values of A/B^2 obtained from the two sets of results are identical within experimental error and equal to 21.2×10^{-12} . Such equality would be expected if the cation is not involved in the surface reaction. For the heterogeneous exchange in methanol¹ $A/B^2 = 208 \times 10^{-12}$ and so $\frac{(A/B^2)_{S_1}}{(A/B^2)_{S_2}} \sim 10$ where S_1 and S_2 denote solvents methanol and n-butanol respectively, *i.e.* $\frac{(k_2 K_2 / K_3)_{S_1}}{(k_2 K_2 / K_3)_{S_2}}$ *ca.* 10.

In the absence of data on K_2 and K_3 in the two solvents it is clearly not possible to place a definite interpretation on this ratio. However, by making a number of assumptions we can give a tentative explanation. We write the ratio on the right-hand side of (2) as

$$\frac{k_2(S_1)}{k_2(S_2)} \times \frac{K_3(S_1)}{K_3(S_2)} \times \frac{K_2(S_1)}{K_2(S_2)}$$

By considering the equilibrium of species between solution and surface then:

$$\frac{K_3(S_1)}{K_3(S_2)} \times \frac{K_2(S_1)}{K_2(S_2)} = \frac{(I^- - A)_{S_1}(I^-)_{S_1}}{(I^- - A)_{S_2}(I^-)_{S_2}} \times \frac{(DNIB)_{S_1}}{(DNIB)_{S_2}} \times \frac{(DNIB - A)_{S_1}}{(DNIB - A)_{S_2}}$$

where $(I^- - A)$ and $(DNIB - A)$ refer to the activities of adsorbed species. The ratio $\frac{(I^-)_{S_1}}{(I^-)_{S_2}}$ is estimated to be *ca.* 30 from the transfer-free-energy as calculated from the Born equation.⁹ The application of the Born equation in this instance is consistent with our earlier application of the Laidler-Eyring equation to the homogeneous reaction. The ratio $\frac{(DNIB)_{S_1}}{(DNIB)_{S_2}}$ is calculated to be *ca.* 3 from solubility measurements¹⁰ and $\frac{(DNIB - A)_{S_1}}{(DNIB - A)_{S_2}}$ is unlikely to differ greatly from unity. For $\frac{(I^- - A)_{S_1}}{(I^- - A)_{S_2}}$, if we regard the adsorbed ion as being

⁹ M. Born, *Z. Phys.*, 1920, 1, 45.

¹⁰ Unpublished work.

capable of 'spreading' its charge then this would be equivalent to an ion of greater radius than iodide. The free energy of transfer of such an ion will be smaller than for iodide, *e.g.* doubling the effective radius will halve ΔG_t , and yield a value for this ratio of *ca.* 1/6.

These considerations lead us to suspect that the observed ratio of 10 arises essentially from the solvent effect on the activity of iodide, and that the surface bimolecular rate constant is not much affected by the transfer from methanol to butanol.

APPENDIX

The Thermodynamic Dissociation Constant of Ammonium Iodide in Methanol, Ethanol, n-Propanol, and n-Butanol.—Methanol. Alkali-metal iodides are highly dissociated in this solvent.¹¹ Ammonium iodide is likely to be similar and we feel justified in putting $\alpha = 1$, see Table 2.

n-Propanol. We have made conductance measurements on ammonium iodide solutions. Application of the Shedlovsky method¹² to these conductance data yields a value of 3.8×10^{-3} mol l⁻¹ (ref. 10) for the dissociation constant at 45 °C.

n-Butanol. The dissociation constant of ammonium iodide in this solvent has been determined at several temperatures² and interpolation gives a value of 9.6×10^{-4} mol l⁻¹ at 45 °C.

Ethanol. A value for the dissociation constant of 9.3×10^{-3} mol l⁻¹ was obtained from the data on other alcohols using an extrapolation based on the theory of Gilkerson¹³ and Fuoss.¹⁴

Estimation of the degree of dissociation. Estimates were made using the equation

$$\log \left(\frac{1 - \alpha}{\alpha} \right) = 2 \log Y_{\pm} + \log (\alpha m) - \log K \quad (1)$$

which is derived directly from the expression for the thermodynamic dissociation constant K . m is the molarity of salt and Y_{\pm} is the mean ionic activity coefficient.

No experimental data are available on activity coefficients so these have been estimated using the Debye-Hückel equation

$$-\log Y_{\pm} = \frac{A(\alpha m)^{\frac{1}{2}}}{1 + Ba(\alpha m)^{\frac{1}{2}}} \quad (2)$$

The constants A and B were calculated using the dielectric constants listed in Table 2. The ion size parameter a was put equal to 3.5×10^{-8} cm for the salt in all solvents.²

Expression (1) was used to calculate α and m for values of the product αm covering the relevant concentration range. Values of α corresponding to the stoichiometric concentrations used in our experiments have been interpolated from large scale plots of α against m .

The Debye-Hückel equation is not strictly applicable for high concentrations and previous work on salts in water and in methanol¹⁵ has shown that the measured mean ionic

¹¹ P. Beronius, G. Wikander, A. M. Nilsson, *Z. phys. Chem.*, 1970, 52, 70.

¹² T. Shedlovsky, *J. Franklin Inst.*, 1938, 225, 739.

¹³ W. B. Gilkerson, *J. Chem. Phys.*, 1956, 25, 1199.

¹⁴ R. Fuoss, *J. Amer. Chem. Soc.*, 1958, 80, 5059.

¹⁵ (a) R. A. Robinson and R. H. Stokes, 'Electrolyte Solutions,' Butterworth, 1959, ch. 9; (b) E. F. Ivanova and V. V. Aleksandrov, *Russ. J. Phys. Chem.*, 1964, 38, 476.

activity coefficients for similar 1 : 1 electrolytes are greater than the Debye-Hückel values. For the two lowest concentrations for which we can calculate reliable values of $k_{2(\text{obs})}$ for the homogeneous exchange in n-butanol *viz.*: $4.88 \times 10^{-3}\text{M}$ and $4.05 \times 10^{-3}\text{M}$, Table 2, equation (2) probably yields fairly reliable value of α and so k_2 is a good approximation although it may still be slightly low.

If we assume that for the higher salt concentration changes in α are primarily responsible for changes in $k_{2(\text{obs})}$, *i.e.* we are neglecting salt effects, then the implication is that α at 0.1M is *ca.* 0.26, much lower than calculated from equation (2). This in turn shows that the Debye-Hückel

value $Y_{\pm} = 0.16$ is much too small compared with $Y_{\pm} = 0.31$ required to satisfy $\alpha = 0.26$. The error is likely to be less severe in the case of propanol and ethanol. We use the calculated α values in these solvents and accept uncertainties of perhaps 50% in the k_2 values (Table 2). Work on the homogeneous exchange cannot be extended to lower concentrations due to interference from the heterogeneous reaction.

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