

where  $\nu$  is the number of ions produced by the dissociation of one molecule,  $R$  is the gas constant,  $\gamma$  the mean molal activity coefficient of the solute, and  $m$  its molality. The heat of transport is the heat which must be removed from a region of solution to which one mole of solute migrates in order to maintain the temperature of that region constant. It is thus a measure of the interaction energy between the solvated ions and their surroundings. Lacking any information on the activity coefficients in our solutions, we computed the heat of transport from Eq. (3) assuming  $\nu = 3$ :

$$Q^* = 3RT^2\sigma \quad \dots(3)$$

This approximation implies that

$$B \equiv 1 + \frac{\partial \ln \gamma}{\partial \ln m} = 1$$

a condition which is fulfilled at infinite dilution but is not necessarily true at any other concentration. The heat of transfer,  $Q^*$ , thus calculated is given along with the value of  $D$  and  $\sigma$  in Table 1.

On interpreting heat of transfer as suggested earlier<sup>9</sup>, a higher value of heat of transport indicates low solvent-solute interaction energy. If this is the situation, the solvent has a poor structure. On comparing the values of heat of transport<sup>9</sup> for  $\text{CdI}_2$  in water, formamide (FM) and methylformamide (MFA), it is apparent that water is the best structured solvent and tetramethylurea the poorest because the order of heat transport is as follows:

$$Q_{\text{TMU}}^* > Q_{\text{MFA}}^* > Q_{\text{FM}}^* > Q_{\text{H}_2\text{O}}^*$$

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### Corresponding Conductance in Aqueous & Non-aqueous Media

J. D. PANDEY & R. P. JAIN

Chemistry Department, University of Allahabad  
Allahabad 211002

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Conductance data in aqueous and non-aqueous media of 1:1 electrolytes have been analysed by the method of corresponding conductance due to Guggenheim. The theoretical values of equivalent conductances at infinite dilutions ' $\Lambda_0$ ' have been obtained. The Walden product has also been calculated on the basis of these results.

GUGGENHEIM<sup>1</sup> developed a simple method of analysing conductivity data of 1:1 electrolytes in aqueous solutions. In the present note Guggen-

heim's corresponding conductance method has been extended for the analysis of conductance data of 1:1 electrolytes in mixed solvents.

Guggenheim's analysis of corresponding conductance is based on Pitts<sup>2-4</sup> equation (1) which contains two adjustable parameters  $\Lambda_0$ , the molar conductance at infinite dilution and  $a$ , the closest distance of a pair of ions for a completely dissociated 1:1 electrolyte as

$$\Lambda = \Lambda_0(1 - \theta c^{1/2}\phi) - \sigma c^{1/2}\Psi \quad \dots(1)$$

In Eq. (1)  $\phi$  and  $\Psi$  are the unspecified functions of  $c$  only and same for all completely dissociated salts, and  $\phi \rightarrow 1$ ,  $\Psi \rightarrow 1$  as  $c \rightarrow 0$ . The constants  $\theta$  and  $\sigma$  are dependent on the nature of the solvent and temperature. For two standard completely dissociated 1:1 salts denoted by the subscripts 1 and 2 having high and low values of  $\Lambda$  respectively Guggenheim derived the expression (2)

$$\Lambda = \Lambda^1 - r(\Lambda^1 - \Lambda^2) \quad \dots(2)$$

Here,  $r$  is independent of concentration. Eq. (2) is known as the principle of corresponding conductance. In Eq. (2) there is only one adjustable parameter,  $r$  and the extrapolation of experimental  $\Lambda$ ,  $\Lambda^1$  or  $\Lambda^2$  value is not required. Guggenheim<sup>1</sup> studied the behaviour of many 1:1 salts, namely KCl, LiCl, NaCl,  $\text{NH}_4\text{Cl}$ , KBr, KI,  $\text{NaBrO}_3$ ,  $\text{LiClO}_4$ ,  $\text{NaClO}_4$ ,  $\text{Me}_4\text{NCl}$ ,  $\text{Me}_4\text{NBr}$  in aqueous media by the method of corresponding conductance and obtained good results.

We have utilized the application of corresponding conductance for the study of 1:1 electrolytes in non-aqueous media. The first set of study concerns with the analysis of the conductances of  $\text{CsClO}_4$ ,  $\text{LiClO}_4$ ,  $\text{RbClO}_4$ ,  $\text{AgClO}_4$ ,  $\text{NH}_4\text{ClO}_4$ ,  $\text{AgNO}_3$  in dimethylformamide. In the second set, we have studied  $\text{KClO}_4$ ,  $\text{LiClO}_4$  and  $\text{NaClO}_4$  in aqueous media also.

The experimental values of conductances of  $\text{LiClO}_4$ ,  $\text{RbClO}_4$ ,  $\text{CsClO}_4$ ,  $\text{AgClO}_4$ ,  $\text{NH}_4\text{ClO}_4$  and  $\text{AgNO}_3$  in dimethylformamide (dielectric constant,  $D = 36.7$ ) and  $\text{KClO}_4$ ,  $\text{LiClO}_4$  and  $\text{NaClO}_4$  in aqueous media at 25°C were taken from Prue-Sherrington<sup>5</sup> and Jones<sup>6</sup> work respectively. By selecting any three of these salts, the single adjustable parameter  $r$  has been calculated. Different values of theoretical conductances at corresponding constant concentrations have been calculated by Eq. (2). Finally, the theoretical values of conductances at infinite dilution  $\Lambda_0$  have been calculated by plotting theoretical conductances against  $\sqrt{c}$  and extrapolating to zero concentration. It enables us to calculate the Walden product,  $\Lambda_0\eta$ . The results are given in Tables 1-3.

Table 2 shows the calculated values of molar conductances of  $\text{CsClO}_4$ ,  $\text{AgClO}_4$  and  $\text{NH}_4\text{ClO}_4$  in dimethylformamide in the concentration range of 0.0001 to 0.0010M. We have chosen two salts  $\text{LiClO}_4$ ,  $\text{RbClO}_4$  as subscripts 1 and 2. The con-

TABLE 1 — CALCULATED VALUES OF CONDUCTANCES AT INFINITE DILUTION AND WALDEN PRODUCT

Electrolyte	$\Lambda_0$	$\Lambda_0\eta$
$\text{CsClO}_4$	86.05	1.628
$\text{AgClO}_4$	87.25	1.650
$\text{NH}_4\text{ClO}_4$	90.31	1.708
$\text{AgNO}_3$	81.35	1.538
$\text{KClO}_4$	140.62	1.247

TABLE 2—CORRESPONDING CONDUCTANCES OF CsClO<sub>4</sub>, AgClO<sub>4</sub>, NH<sub>4</sub>ClO<sub>4</sub>, AgNO<sub>3</sub> IN DIMETHYLFORMAMIDE AT 25°C  
(ohm<sup>-1</sup> cm<sup>-2</sup> mole<sup>-1</sup>)

	Concentration (M)								
	0.0001	0.0002	0.0003	0.0004	0.0006	0.0008	0.0010	0.0015	0.0019
LiClO <sub>4</sub> (exp)	75.76	74.98	74.61		73.69		72.61		
RbClO <sub>4</sub>	82.71	82.08	81.80		80.76		79.59		
CsClO <sub>4</sub> *	84.67	84.13	83.90						
	(84.6698)	(84.0509)	(83.5532)		(82.7226)		(81.5276)		
AgClO <sub>4</sub> (exp)†	85.83	85.02	84.548		83.65				
	(85.8298)	(85.2174)	(84.97772)		(83.8842)		(82.6744)		
NH <sub>4</sub> ClO <sub>4</sub> (exp)‡	89.00		86.69						
	(88.9997)	(88.4053)	(88.2055)		(87.0586)		(85.8084)		
KI (exp)				79.69		78.48		77.19	76.43
KBr				80.74		79.59			77.16
AgNO <sub>3</sub> (exp)§				77.06		70.67		64.02	
				(77.0601)		(75.7349)		(74.16)	

Calc. values in parentheses assuming \* $r=1.2776$ ; † $r=1.4419$ ; ‡ $r=1.8909$ ; § $r=2.5047$ .

 TABLE 3 — CORRESPONDING CONDUCTANCE OF KClO<sub>4</sub> IN AQUEOUS MEDIA AT 25°C (ohm<sup>-1</sup> cm<sup>-2</sup> mole<sup>-1</sup>)

	Concentration (M)								
	0.0005	0.001	0.002	0.005	0.010	0.020	0.050	0.070	0.100
LiClO <sub>4</sub> (exp)	104.18	103.44	102.46	100.57	98.61	96.18	92.20	90.50	88.56
NaClO <sub>4</sub>	115.64	114.87	113.80	111.75	109.59	106.96	102.40	100.52	98.43
KClO <sub>4</sub> (exp)*	138.76	137.87	136.62	134.16	131.46	127.92	121.62	118.79	115.20
	(138.75)	(137.92)	(136.67)	(134.30)	(131.74)	(128.64)	(122.97)	(120.73)	118.3417

\*Calculated values in parentheses assuming  $r=3.0174$ .

ductance study of AgNO<sub>3</sub> in dimethylformamide has been done in the concentration range of 0.0004 to 0.0019M by choosing KI and KBr as the subscripts 1 and 2. Finally theoretical values of conductance have been calculated in the case of KClO<sub>4</sub> (Table 3) in the conc. range of 0.0005 to 0.100M. The results are in good agreement with the experimental values. Theoretical values of  $\Lambda_0$  and Walden product  $\Lambda_0\eta$  obtained for these salts are shown in Table 1.

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#### Studies on the Cell Ni|Ni-Soap(s), K-Soap, Cu-Soap(s)|Cu

WAHID U. MALIK & AJAY K. JAIN

Department of Chemistry, University of Roorkee, Roorkee

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The e.m.f., temperature coefficient of e.m.f. and the thermodynamic parameters of the cell reaction have been computed for the cells of the type Ni|Ni-soap(s), K-soap, Cu-soap(s)|Cu. The soaps have been derived from lauric, myristic, palmitic and stearic acids. The cell's reaction is accompanied by decrease in enthalpy as well as entropy. The cell e.m.f. is also found to be independent of concentration of potassium soap solution.

IN continuation of our earlier work<sup>1-5</sup> on metal-metal soap electrode system, the e.m.f. of the cell of the type (A) has been evaluated.

Ni|Ni-soap(s), K-soap, Cu-soap(s)|Cu (A)

Potassium salts of lauric (C<sub>11</sub>), myristic (C<sub>13</sub>), palmitic (C<sub>15</sub>) and stearic (C<sub>17</sub>) acids were prepared from reagent grade (BDH) acids and crystallized from ethanol.

Nickel and copper soaps were prepared by a direct metathesis reaction at 50-55° from the corresponding potassium soaps and aqueous solution of nickel or copper sulphate. The precipitated soaps were washed with distilled water and then with ethanol to remove free precipitant. The soaps gave satisfactory elemental analysis.

Nickel electrodes were prepared by depositing nickel on platinum wires by the electrolysis of a solution containing nickel sulphate (15%), boric acid (1%) and sodium chloride (0.6%). The electrodes were connected to a 4 V battery and a current of 20 mamp was passed for about 2 hr. Copper electrodes were prepared by depositing copper on platinum wires by the electrolysis of a solution containing CuSO<sub>4</sub> (8%) and H<sub>2</sub>SO<sub>4</sub> (4.6%). The electrodes were connected to a 2 V battery and a current of 15 mamp was passed for 4 hr.

A Cambridge portable potentiometer was used for e.m.f. measurements of the cell of the type (A) at different temperatures. The cell vessel employed was of H type. The two limbs of the cell were provided with nickel and copper electrodes. The cell contained aqueous solution of potassium soap saturated with nickel and copper soaps. Some solid metal soaps were always added to the cell to make certain that potassium soap solution was saturated with respect to metal soaps.