TABLE 1 — D VALUES (FROM EQ. 1) AND SURFACE AREAS OF VARIOUS CARBONS OBTAINED BY TWO METHODS

Carbon	$D \times 10^{-2}$ (Eq. 1)	Surface area (m^2/g)	
		From Dubinin plots	From BET (N_2) method (ref. 15)
Mogul	14·09	324	308
Mogul A	14·00	252	228
ELF-0	14·61	209	171
Spheron-4	15·09	224	153
Spheron-6	15·58	138	120
Spheron-9	14·76	151	115
Spheron-C	15·65	288	254
Philblack-I	15·95	103	117
Philblack-E	17·80	132	135
Philblack-A	24·39	46	46
Graphon	25·00	91	76
Kosmos-40	19·01	33	31
Sugar charcoal	14·31	338	337*
Activated carbons			
A	18·01	1148	1093*
B	18·72	1005	987*
C	19·83	955	821*
D	18·98	794	738*
E	19·81	550	505*

*Values obtained in the laboratories of Fertilizer Corporation of India, Sindri, for which the authors are thankful to Shri V. K. Puri.

TABLE 2 — EFFECT OF DEGASSING CHARCOAL AND A FEW CARBON BLACKS ON D AND SURFACE AREA VALUES AS OBTAINED FROM DUBININ PLOTS

Carbon	Degassed at 600°		Degassed at 1000°	
	$D \times 10^{-2}$	Surface area (m^2/g)	$D \times 10^{-2}$	Surface area (m^2/g)
Sugar charcoal	17·56	660	17·52	323
Mogul-A	14·58	240	14·74	182
Mogul	14·23	295	15·28	239
ELF-0	14·73	189	15·45	166
Spheron-4	15·43	192	15·72	130

600°, which is known to cause elimination of tarry matter as well as combined oxygen capable of evolving carbon dioxide[12], causes a considerable rise in surface area, evidently due to availability of additional space previously blocked by these species. The adsorbate interaction, however, decreases as indicated by the rise in value of D, due to widening of capillary pores. The same treatment when extended to carbon blacks, on the other hand, causes a slight fall in surface area. These blacks are essentially free of tarry matter but they do contain 0·6 to 2·2% oxygen which comes off as carbon dioxide on degassing at 600° (ref. 13). It appears that this oxygen, in the case of carbon blacks, is not present within the micropores. This view is also supported by the fact that there is no significant rise in the value of D in the case of carbon blacks.

The appreciable fall in surface area on degassing sugar charcoal as well as each of the carbon blacks at 1000° appears to be due to shrinkage in pore structure as has been observed by Toda et al.[14] in the case of coals.

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Viscosity of Cesium Chloride in Ethylene Glycol

R. L. BLOKHRA & Y. P. SEHGAL

Department of Chemistry, Himachal Pradesh University Simla 171001

The viscosities of cesium chloride solutions in ethylene glycol at concentrations varying from $6·8 \times 10^{-3} M$ to saturation and at temperatures 25°, 30° and 40° are reported. The results are interpreted in terms of structure breaking capacity of the electrolyte by evaluating the temperature coefficient of constant-B of the Jones-Dole equation. The activation energy of the viscous flow is calculated from the Arrhenius equation.

IT has been found by number of workers[1] that the addition of an electrolyte could either break or make the structure of a liquid. Since viscosity is a property of liquids which depends on the intermolecular forces, the structural aspects of liquids can be inferred from the viscosity of solutions at different concentrations and temperatures. With the development of the interionic theory, much of the interest in the subject has been directed towards accurate determination of the viscosities of very dilute solutions of electrolytes and the theoretical interpretation of the results. The aim of the present study is to determine the viscosity of solutions of cesium chloride in ethylene glycol at different temperatures and concentrations of the electrolyte and to analyse the data in terms of Jones-Dole equation[2] (1)

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

where C is the molar concentration and A and B are the constants representing the contribution from interionic electrostatic forces[3] and ion-solvent interaction respectively. Structure breaking capacity of the electrolyte and effect of temperature on the coefficient B have also been studied.

Analar grade anhyd. and recrystallized cesium chloride was used. Ethylene glycol dried over calcium oxide and calcium sulphate was distilled under reduced pressure, dried over sodium metal under reflux for 7-10 hr, and redistilled under reduced pressure. The solvent thus purified had the following physical constants at 25°C: specific conductance, 8×10^{-7} ohm^{-1} cm^{-1}; density, 1·1094 g ml^{-1} and viscosity, 0·170 poise, which are in excellent agreement with the literature[4] values.

Solutions were prepared by weight under dry conditions. Conversion between equivalent concentration and molality was made following the relationship[5]

$$m = 1/(d/M - M_2/1000) \qquad \ldots(2)$$

where M is the molarity, m is molality, d is the density of the solution and M_2 is the molecular weight of the electrolyte.

The viscosities (Table 1) and densities of the solutions at different concentrations and temperatures were determined by the method described earlier[6,7]. All measurements were carried out in a thermostat having an accuracy of $\pm 0.05°C$. The viscosities and densities of the solutions are reproducible within ± 0.0001 unit.

It appears from Table 1 that viscosity of CsCl solutions decreases with the increase in temperature. The plots of (η) versus [cesium chloride] in ethylene glycol at all temperatures reported here were linear thereby indicating the applicability of Eq. (1).

The values of B were determined from the slope of the linear plots of $(\eta/\eta_0 - 1)/C^{1/2}$ versus $\sqrt{C}$, and were 1·66, 2·33 and 3·09 at 25°, 30° and 40° respectively. These values show that coefficient-B

TABLE 1 — VISCOSITY OF CESIUM CHLORIDE SOLUTIONS IN ETHYLENE GLYCOL AT DIFFERENT TEMPERATURES AND CONCENTRATIONS

[CsCl] $\times 10^2$ (M)	$\eta \times 10^2$ (poise)	Relative viscosity η/η_0
TEMPERATURE 25°		
1·322	16·69	0·982
1·490	16·70	0·982
1·869	16·73	0·984
2·438	16·80	0·988
2·890	16·81	0·989
3·223	16·84	0·991
3·794	16·93	0·996
TEMPERATURE 30°		
0·681	13·41	1·001
0·824	13·44	1·004
1·000	13·48	1·006
1·123	13·52	1·010
1·398	13·56	1·012
1·690	13·62	1·017
2·084	13·69	1·022
TEMPERATURE 40°		
2·634	9·26	0·917
3·062	9·26	0·917
3·406	9·31	0·922
4·284	9·32	0·923
4·860	9·36	0·927

TABLE 2 — VALUES OF $E\eta$ FOR CESIUM CHLORIDE IN ETHYLENE GLYCOL

$C \times 10^2$ (M)	$E\eta \times 10^{-4}$ J mole^{-1}
1·00	1·39
2·00	1·44
3·00	1·33
4·00	1·33
Saturated solution	1·40

increases with increasing temperature. Recently, it has been emphasized[8] that the sign of the temperature coefficient of B is a better criterion[9,10] than the magnitude of B itself for determining the solute-solvent interaction, and accordingly electrolytes which are structure makers will have negative values of dB/dT and structure breakers will have positive values. In the present study, the values of dB/dT for cesium chloride in ethylene glycol are positive showing that cesium chloride has a structure breaking tendency. Further, the positive values of B can be attributed to the large size of the ions. The values of coefficient-A decreased with increasing temperature.

Table 1 also shows that viscosity at a particular [CsCl] decreases with the rise in temperature, and it can be represented in all the cases by Eq. (3)

$$\eta = Ae^{E\eta/RT} \qquad \ldots(3)$$

where A and E_η are the constants for a given solution. By analogy with the Arrhenius theory of reaction rates, E_η, which has the dimensions of work, can be regarded as the activation energy for viscous flow[11]. Furthermore, E_η is related to the work[12] required to form vacant sites in the solvent matrix. A greater value of E_η will indicate that greater energy is required to break the solvent structure. The values of E_η for cesium chloride in ethylene glycol at different concentrations were calculated from the slopes of the linear plots of log η versus $1/T$, and are given in Table 2.

Since E_η is the amount of work required to form vacant sites in the solvent matrix, Table 2 shows that this work is about 1.4×10^4 J mole^{-1} and appears to be independent of the [electrolyte].

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Heats of Formation & Lattice Energies of α-, β- & γ-Picoline Complexes of Copper Fluoborate

A. CHATTERJEE & G. C. BHATTACHARYA

Department of Chemistry, St Xavier's College, Ranchi
and
Chemistry Department, Ranchi University, Ranchi

Kapustiniskii's equation and a thermochemical cycle have been employed for the determination of lattice energy of α-, β- and γ-picoline complexes of copper fluoborate. The divergent results obtained for a particular complex by the two methods do not permit an assessment of stability order of comparable complexes.

HEATS of formation and lattice energies of β- and γ-picoline complexes of Co, Zn and Cd fluoborate have been already reported by Bhattacharya and Dasgupta[1]. In this note heats of formation and lattice energies of α-, β- and γ-picoline complexes of copper fluoborate have been determined. In each case three readings were taken and the mean has been reported. Heats of formation (Q) determined by applying[1] Hess's law of heat summation are 197·83, 230·85 and 237·97 kJ mole^{-1} for $Cu(BF_4)_24\alpha$-Pic, $Cu(BF_4)_24\beta$-Pic and $Cu(BF_4)_24\gamma$-Pic respectively.

Calculation of lattice energy — Of the available equations[2] for the calculation of lattice energy that of Kapustiniskii[3] was found simple. In a second attempt, use was made of a thermochemical cycle[4].

The expression: $U_2 = U_1 + Q - E$ where U_2 = lattice energy of complex salt, U_1 = lattice energy of simple salt, Q = heat of formation of the complex salt and E = coordination energy. U_1 is evaluated from Kapustiniskii's equation, Q is experimentally determined and E is theoretically calculated from the equation of Yatsimirskii[5]. The values thus found from Kapustiniskii's equation and from thermochemical cycle consideration are given in Table 1.

TABLE 1 — LATTICE ENERGY OF THE COMPLEX SALTS

Compound	U_2 (kJ/mole)	
	Kapustiniskii	Thermochemical cycle
$Cu(BF_4)_24\alpha$-Pic	1093·97	1280·79
$Cu(BF_4)_23\alpha$-Pic	1017·95	1303·81
$Cu(BF_4)_22\alpha$-Pic	935·50	1332·65
$Cu(BF_4)_24\beta$-Pic	1093·97	1276·31
$Cu(BF_4)_23\beta$-Pic	1017·95	1305·03
$Cu(BF_4)_22\beta$-Pic	935·50	1318·26
$Cu(BF_4)_24\gamma$-Pic	1093·97	1272·75
$Cu(BF_4)_23\gamma$-Pic	1017·95	1312·90
$Cu(BF_4)_22\gamma$-Pic	935·50	—

The data in Table 1 show that the application of lattice energy to assess the stability order of comparable complexes may not be helpful, since the values of U_2 obtained using Kapustiniskii's equation and thermochemical cycle differ widely even for the same complex. Similar divergent values have been reported by Bhattacharya and Dasgupta[1] in their work on β- and γ-picoline complexes of Co, Ni and Zn fluoborates. This large discrepancy in values has been reported[6] for the compounds like $[Fe(NH_3)_6]Cl_2$ and $[Mn(NH_3)_6]Cl_2$.

According to Kapustiniskii's equation, the lattice energies of the three systems 4, 3 and 2 of a particular compound decrease in this order, whereas reverse is true when lattice energies are obtained by the application of thermochemical cycle. The heat of formation cannot be found out with any fair degree of accuracy and hence there is uncertainty in the evaluation of lattice energy by thermochemical methods. Keeping in view the results of the present and previous work, it may be inferred that the determination of the lattice energies with present forms of equations cannot be helpful to assess the stability of the complex compounds.

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Polymerization of Methyl Methacrylate by Ammonium Hexachlororhodate(III)

M. M. TAQUI KHAN & Q. ANWARUDDIN

Departments of Chemistry, Indian Institute of Technology Madras 600036 and Nizam College, Hyderabad 500001

The kinetics of Rh(III)-catalysed polymerization of methyl methacrylate were studied under strictly deaerated conditions at 60°±0·1°C. The rate of polymerization was measured by a gravimetric determination of the monomer disappearance. Monomer and catalyst concentrations were varied, and the rate of polymerization was found to be proportional to [monomer]$^{2·5}$ and [catalyst]$^{0·35}$. The chain lengths of the various PMMA samples obtained in the experiments were determined by a measurement of their viscosities in benzene solutions. In the light of the experimental results, a tentative initiation step for polymerization was proposed.

RHODIUM salts have been recently used as catalysts in the polymerization of butadiene[1,2] and methyl acrylate[3]. In the Rh^{3+}-catalysed polymerization of butadiene, the polymer had a high steric purity and any chance of random free radical type of polymerization was inhibited by Rh^{3+}. The conditions for the polymerization of butadiene, however, varied vastly from one rhodium