

TABLE 1 — DIPOLE MOMENTS AND MOLAR CONCENTRATIONS OF *gauche* AND *anti* FORMS OF 1,2-DIBROMOETHANE IN DIFFERENT SOLVENTS

Solvent	$\mu(D)$	$\mu_g(D)$	X_g	X_t	ΔE (kcal mole ⁻¹)
Cyclohexane	0.98	2.94	0.112	0.888	1.66
Benzene	1.33	2.94	0.204	0.796	1.23
Toluene	1.00	2.94	0.115	0.885	1.64
<i>o</i> -Xylene	1.00	2.94	0.115	0.885	1.64
<i>m</i> -Xylene	1.19	2.94	0.164	0.836	1.39
<i>p</i> -Xylene	1.16	2.94	0.155	0.845	1.43

g = *gauche* form; t = *anti* form.

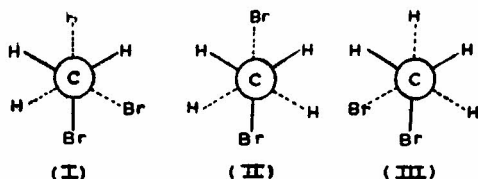


Fig. 1 — Different conformations of 1,2-dibromoethane

dipole moment at any temperature is given by

$$\mu = \mu_g(x_g)^{\frac{1}{2}} \quad \dots(8)$$

where x_g is the mole fraction and μ_g the dipole moment of the *gauche* form present. If ΔE is the energy difference between the *anti* and *gauche* forms, then

$$x_g/x_t = 2 \exp(-\Delta E/RT) \quad \dots(9)$$

where x_t is the mole fraction of the *anti* (*trans*) form. The values of x_g and x_t were calculated from Eq. (8) and ΔE values were calculated from Eq. (9).

The values of x_g , x_t and ΔE for 1,2-dibromoethane in cyclohexane, benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene are recorded in Table 1.

From Table 1, it is evident that at equilibrium, *anti* form predominates over the *gauche* form in these solvents. The energy difference between the *anti* and *gauche* forms is between 1 and 2 kcal mole⁻¹ in all these systems. The energy difference between the *anti* and *gauche* forms of 1,2-dichloroethane was found to be 1.21 kcal mole⁻¹ (ref. 13). The energy difference between *anti* and *gauche* forms of 1,2-dibromoethane in toluene, *o*-xylene and *m*-xylene may not be absolute as dipole moments of toluene (0.33 D), *o*-xylene (0.52 D) and *m*-xylene (0.32 D) might be affecting the dipole moment of 1,2-dibromoethane.

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Physicochemical Studies in Non-aqueous Solvents: Part XVII — Cryoscopic Studies of Some Uni-valent Electrolytes in Tetramethylurea

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Cryoscopic measurements of nine 1:1 electrolytes have been carried out in tetramethylurea (TMU) in the concentration range $4.5\text{--}86.9 \times 10^{-3}$ mol kg⁻¹. A modified Lewis-Randall equation has been used to obtain activity coefficients (γ_{\pm}) of these salts. For comparison between electrolytes, activity coefficients at 0.01, 0.03 and 0.05 mol kg⁻¹ have been computed from the plots of γ_{\pm} against molality. The results at 0.05 mol kg⁻¹ have also been compared with those of the same electrolytes in formamide, hexamethylphosphotriamide and water. The lower values of activity coefficients in TMU than those in the above-mentioned solvents indicate associated nature of these salts in TMU.

STUDIES in non-aqueous solvents are gaining considerable attention recently¹. We have earlier reported the results of cryoscopic studies in formamide (F)² and hexamethylphosphotriamide (HMPT)³ as solvents. Conductance^{4,5}, transference number⁶ and thermochemical⁷ measurements in tetramethylurea (TMU) have thrown considerable light on the behaviour of various salts in this solvent. However, cryoscopic studies in this solvent are not yet reported. TMU has a convenient freezing point (-1.2°) and a number of electrolytes are soluble in it at this temperature. It is, therefore, worth while investigating electrolytic solutions of TMU cryoscopically.

Tetramethylurea (Fluka AG) was purified as reported⁸ (b.p. $76.5^{\circ}\text{C}/12$ mm, sp. cond. 2.5×10^{-8} ohm⁻¹ cm⁻¹, density 0.9616 g cm⁻³ and viscosity

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TABLE 1 — VARIOUS PARAMETERS FOR ACTIVITY COEFFICIENTS (γ_{\pm}) OF SOME 1:1 ELECTROLYTES IN TETRAMETHYLUREA FROM FREEZING POINT DATA

m	ΔT	$j/m^{1/2}$	γ_{\pm}
LiClO ₄			
0-00397	0-040	0-5714	0-88
0-01548	0-155	0-3293	0-83
0-02418	0-240	0-3172	0-81
0-04243	0-415	0-3068	0-77
0-05717	0-555	0-2936	0-75
NaClO ₄			
0-01897	0-190	0-2954	0-88
0-03649	0-360	0-2884	0-84
0-05561	0-545	0-2600	0-82
0-07502	0-730	0-2482	0-81
0-08408	0-815	0-2469	0-80
NaSCN			
0-01299	0-125	0-6868	0-78
0-02686	0-255	0-5534	0-72
0-04032	0-380	0-4846	0-69
0-05604	0-520	0-4698	0-65
0-08094	0-740	0-4369	0-62
KClO ₄			
0-00949	0-095	0-4229	0-86
0-02716	0-265	0-3974	0-80
0-04088	0-395	0-3689	0-78
0-05555	0-530	0-3657	0-75
0-07535	0-710	0-3552	0-72
KSCN			
0-01078	0-105	0-6464	0-80
0-02799	0-265	0-5571	0-72
0-03787	0-355	0-5252	0-69
0-06969	0-635	0-4822	0-66
0-08363	0-760	0-4481	0-65
CsClO ₄			
0-00915	0-090	0-6115	0-82
0-01437	0-140	0-5608	0-78
0-02769	0-265	0-5009	0-73
0-03920	0-370	0-4851	0-70
0-07322	0-665	0-4806	0-66
NH ₄ ClO ₄			
0-01144	0-110	0-7458	0-78
0-02366	0-220	0-7120	0-70
0-04064	0-370	0-6349	0-65
0-05985	0-530	0-6206	0-60
0-08688	0-745	0-6064	0-55
Me ₄ NClO ₄			
0-00550	0-055	0-5805	0-88
0-00911	0-090	0-5696	0-84
0-01434	0-140	0-5421	0-81
0-02021	0-195	0-5350	0-79
0-02449	0-235	0-5171	0-77
Pr ₄ NClO ₄			
0-00450	0-045	0-6323	0-87
0-00965	0-095	0-5879	0-84
0-01653	0-160	0-5700	0-80
0-02464	0-235	0-5532	0-77
0-03519	0-330	0-5427	0-63
0-04469	0-415	0-5230	0-62

TABLE 2 — ACTIVITY COEFFICIENTS (γ_{\pm}) OF SOME 1:1 ELECTROLYTES IN TMU AND OTHER SOLVENTS AT VARIOUS CONCENTRATIONS

Salt	γ_{\pm}					
	TMU (m)			F (0-05m)	HMPT (0-05m)	H ₂ O (0-05m)
	0-01	0-03	0-05			
LiClO ₄	0-87	0-78	0-75	0-95	0-79	0-85
NaClO ₄	0-93	0-85	0-82	0-94	0-79	0-82
NaSCN	0-80	0-70	0-66	0-95	—	0-79†
KClO ₄	0-88	0-79	0-76	0-94	0-76	0-85*
KSCN	0-82	0-71	0-68	0-97	0-72	0-77†
CsClO ₄	0-83	0-72	0-68	0-93	0-74	—
NH ₄ ClO ₄	0-79	0-68	0-62	0-90	0-62	—
Me ₄ NClO ₄	0-84	0-76	0-72	0-94	0-72	—
Pr ₄ NClO ₄	0-83	0-75	0-70	—	—	—

*Values at 0-02 m .
†Values at 0-01 m at 25°.

1.404 × 10⁻²P). The electrolytes used were prepared and/or purified by the methods already reported⁸.

Freezing points of the various electrolytic solutions for cryoscopic studies were measured by the procedure described earlier².

The molal freezing point depression constant (K_f) has been determined using solutions of doubly distilled aniline (AR, b.p. 184.5°) and triply distilled carbon tetrachloride (AR, b.p. 76.8°) of different concentrations. Plots of ΔT versus m for both the solutes are linear and molal freezing point depression constant of TMU as obtained from the plots⁹ is 5.22 ± 0.02 mol⁻¹ kg*.

Cryoscopic measurements of lithium, sodium, potassium, cesium, ammonium, tetramethylammonium and tetrapropylammonium perchlorates and sodium and potassium thiocyanates have been carried out in the concentration range 4.5-86.9 × 10⁻³ mol kg⁻¹. The activity coefficients (γ_{\pm}) of these salts have been obtained as reported² from the modified form of Lewis-Randall equation¹¹ (Eq. 1).

$$\log \gamma_{\pm} = -\frac{j}{2.303} - \frac{2}{2.303} \int_0^m \frac{j}{m^{1/2}} d(m^{1/2}) \quad \dots(1)$$

The plots of $j/m^{1/2}$ versus $m^{1/2}$ are smooth curves and the integral in the equation has been evaluated by measuring the areas under the curves within specific limits. The values of m , ΔT , j , $m^{1/2}$ and γ_{\pm} at each concentration for all the electrolytes are given in Table 1.

Table 1 reveals that the activity coefficients (γ_{\pm}) for all the electrolytes decrease with increasing

*Zordon and coworkers¹⁰ have determined the enthalpies of melting (ΔH_m) of TMU to be 3.37 ± 0.02 kcal mol⁻¹. Molal freezing point depression constant (K_f) as calculated from this value is 5.07 mol⁻¹ kg. However, in view of the purity of materials used, and precautions taken during the experiments to avoid moisture, the present value may be considered more reliable.

concentration. Similar activity coefficient-concentration dependence has also been noticed in many other solvents². For comparison between the electrolytes, the activity coefficients have been obtained at molalities 0.01, 0.03 and 0.05 from the plots of γ_{\pm} against m . These values are recorded in Table 2.

It is clear from Table 2 that values of γ_{\pm} of the electrolytes with common anion (except lithium and ammonium perchlorates) decrease with increasing size of the cation. This behaviour is in accord with the solvating properties of the ions⁴⁻⁶. However, γ_{\pm} of lithium and ammonium perchlorates are relatively lower than expected. Conductance and thermochemical studies have also shown the abnormal behaviour of lithium and ammonium salts in TMU. In HMPT³ and F² also, γ_{\pm} values of lithium and ammonium salts are low. The behaviour of these salts may be attributed to the imperfect solvation of lithium and ammonium ions.

Due to the lack of sufficient cryoscopic data, the general trend cannot be predicted for the electrolytes with common cations. However, it is apparent from Table 2 that γ_{\pm} of sodium and potassium thiocyanates are lower than those of the corresponding perchlorates in contrast to the behaviour of these salts in F and HMPT. Barker and Caruso⁴ have shown from conductance studies that sodium thiocyanate is associated whereas sodium perchlorate is completely dissociated in TMU. The lower γ_{\pm} values of thiocyanates have been explained to be due to associated nature of thiocyanates in this solvent.

For the sake of comparison between solvents, γ_{\pm} values at 0.05 m have also been included in Table 2 for F², HMPT³ and water¹². Table 2 reveals that γ_{\pm} values in TMU are lower than those in water, F and HMPT (even though the dielectric constant of TMU and HMPT are nearly equal). Since conductance⁴ and thermochemical studies⁷ indicate ion-pair formation in this solvent, low γ_{\pm} values obtained in the present studies are in accord with the earlier observations.

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Oxidation Studies: Part XII — Effect of (Ag⁺ + Cu²⁺) on Oxidation of Acetic, Propionic, Isobutyric & Pivalic Acids by Ce⁴⁺ in Sulphuric Acid Medium

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The rate of Ag⁺-catalysed oxidation of organic acids was found to be significantly higher when Cu²⁺ was added to the system under otherwise similar conditions. The rate law in the presence of (Ag⁺ + Cu²⁺) mixture was same as in the presence of Ag⁺ alone. The order of [Ce⁴⁺] was found to be unity and that of [Ag⁺] and [organic acid] fractional. Keeping [Ag⁺] and ionic strength (μ) constant, an increase in [Cu²⁺] did not affect the rate. A mechanism in which the radicals produced are trapped and oxidized by Cu²⁺ has been proposed to explain the results.

IN the oxidation of organic substrates by Ce⁴⁺, Ag⁺ and Cu²⁺ were found to be better catalysts among the various transition metal ions employed as catalysts^{1,2}. It is known that Cu²⁺ acts as a good radical trap specially when primary and secondary alkyl radicals are produced in the system³⁻⁵. The catalytic effect of (Ag⁺ + Cu²⁺) mixture was found to be decidedly greater than that of Ag⁺ alone and hence, a detailed kinetic study was undertaken to understand the mechanistic aspects of (Ag⁺ + Cu²⁺) catalysed oxidation of acetic, propionic, isobutyric and pivalic acids.

All the chemicals used were of AR grade. The kinetics runs were carried out as described earlier⁶. The products of oxidative decarboxylation of aliphatic acids were identified by spot tests as carbon dioxide⁷ and corresponding alcohol⁸.

Under pseudo-conditions order with respect to [Ce⁴⁺] was unity as revealed by the linear plots of $\log \left[\frac{a}{a-x} \right]$ vs time (Fig. 1A). The order with respect to [organic acid] and [Ag⁺] were fractional (Figs. 1B and 1C). Keeping [Ag⁺] and ionic strength (μ) constant, increase in [Cu²⁺] did not affect the k_{obs} values. However, the k_{obs} values in the presence of (Ag⁺ + Cu²⁺) were much greater than those obtained in the presence of Ag⁺ alone or in uncatalysed reaction (Table 1) under otherwise similar conditions. The reaction was studied in the temperature range 45-60°. The fractional order with respect to [organic acid] indicates that it might be involved in complex formation either with Ce⁴⁺ or Ag⁺. Spectral studies in the present work do not indicate any complex formation between Ce⁴⁺ and organic acid, in conformity with our earlier observations⁶. This as well as the effect of [H⁺], [sulphate] and [bisulphate], which show a similar trend reported earlier for other substrates, indicate that neutral Ce(SO₄)₂ is the reactive species. As all organic acids follow a similar rate law and hence