In Scheme 1 ΔH_g° is the sum of coordination bond energies of four acetato groups around a thorium atom. The standard heat of formation of thorium[4] is 598 ± 6 kJ mol^{-1}. The standard heat of formation of neutral acetate radical[4] is -207.5 ± 4 kJ mol^{-1}. Tetraacetatothorium(IV) sublimes to give monomer in the gas phase. Assuming the standard heat of sublimation ΔH_5, of ThAc$_4$ (c) $= 50$ kJ mol^{-1}, this yields the heat of complexation of ThAc$_4$(g) $= -2392 \pm 10$ kJ mol^{-1}. The acetate being a bidentate ligand, the (Th - O) bond strength is one-eighth of ΔH_g and is thus equal to 299 kJ mol^{-1} or 71.5 kcal mol^{-1}.

Similarly, the U-O bond strength in tetraacetatouranium(IV) can be calculated. From Thakur et al[7]. ΔH_f° UAc$_4$(c) $= -2493 \pm 5$ kJ mol^{-1}; from Weast[4], ΔH_f° U(g) $= 527 \pm 13$ kJ mol^{-1} and assuming ΔH_s° UAc$_4$(s) $= 50$ kJ mol^{-1}, we get (U - O) bond strength in UAc$_4$ equal to 267 kJ mol^{-1} or 63.8 kcal mol^{-1}. It is observed that the metal-oxygen bond strength falls from thorium to uranium.

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Excess Free Energy of Binary Mixtures of Isomeric Butanols With n-Heptane†

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The excess free energy of mixing (GE) has been calculated from isothermal vapour-liquid equilibrium data of binary mixtures of isomeric butanols with n-heptane at 75°C. A recirculating equilibrium still has been used for the measurement of the vapour-liquid equilibria of binary mixtures at constant temperature. The decreasing values of GE from n- to tert-butanol indicate the pronounced effect of branching of alkyl chain in butanols on GE.

IN continuation of earlier work from our laboratory on the measurements of excess volumes of binary mixtures of isomeric butanols with n-heptane, the excess free energies of these binary mixtures have now been determined at 75°C with a view to investigating the nature of interactions and the effect of alkyl chain of butanol on breaking of hydrogen bonds.

The compounds used and the methods of their purification have been described in an earlier communication[1]. The purities of compounds were checked by GLC and found to be more than 99.5%.

The appartus used to determine the vapour-liquid equilibria was a modified Jones-Colburn recirculating still[2], since it was possible to obtain a thermal equilibrium in 30 min as well as conduct experiment with about 25 ml of liquid mixture. The system pressure in the still was adjusted to a desired value by connecting the still to the vacuum line via manometer and micrometer needle regulating valve. The pressure was determined from the difference of barometer reading after appropriate correction for expansion of mercury and from the difference in room temperature and the temperature of calibration of the cathedometer used. The uncertainty in temperature of $\pm 0.1°C$ caused an uncertainty in pressure measurement of ± 0.2 mm. The vapour and liquid samples were analysed by a calibrated pyknometer. The mole fractions were accurate to within ± 0.0009.

The vapour pressure results are given in Table 1 as a function of liquid mole fraction x_1 of n-heptane and the corresponding mole fraction in the vapour phase y_1.

Since the experimental values of the second virial coefficients for compounds at 75° were not available in the literature, the same were calculated by well known Pitzer-Curl equation[3] and are listed in Table 2 along with molar volumes V^L. The liquid phase coefficients ν_1 and ν_2 were calculated by the usual formulae[4].

The accuracy of the data was checked by Herington's thermodynamic consistency test[5]. The data are consistent within 1.4, 6.9, 1.6 and 1.9% in the case of n-, iso-, sec- and tert- butanol systems. The binary mixtures of n-heptane with n-, iso-, sec- and tert- butanols form azeotropes at 0.81, 0.72., 0.62 and 0.35 mole fractions of n-heptane.

The calculated values of excess free energy G^E from isothermal vapour liquid equilibrium for these systems are listed in Table 1. The curves may be drawn following a best fit to an equation of the form

$$G^E/RT = x(1-x) \sum_{n=1}^{4 \text{ or } 5} A_n (1-2x)^{n-1}$$

Where x is the mole fraction of n-heptane in the liquid phase. The values of coefficients A_n along with standard deviation σ calculated by Honeywell 400 computer are listed in Table 3. The n- and iso-butanol systems curves are found to be best fit by a four-constant equation while those of sec- and tert- butanols by a five-constant equation.

TABLE 1 — VAPOUR-LIQUID EQUILIBRIUM DATA OF n-HEPTANE (1) + ISOMERIC BUTANOL (2) BINARY MIXTURES AT 75°

Mole fraction of n-heptane		P in mm	v_1	v_2	G^E (Jmol⁻¹)	Mole france of n-heptane		P in mm	v_1	v_2	G^E (Jmol⁻¹)
In liquid	In vapour					In liquln	In vapour				

n-Heptane (1) + n-butanol (2) system — $p_1 = 361.3$ mm, $p_2 = 128.7$ mm
(and right) n-Heptane (1) + sec-butanol (2) system — $p_1 = 361.3$ mm, $p_2 = 278.9$ mm

In liquid	In vapour	P in mm	v_1	v_2	G^E	In liquln	In vapour	P in mm	v_1	v_2	G^E
0.0462	0.3830	198.1	4.590	0.9926	225	0.0748	0.2535	349.8	3.283	1.008	277
0.0668	0.4634	232.7	4.500	1.106	378	0.1373	0.3638	385.9	2.826	1.015	450
0.1125	0.5700	288.4	4.062	1.076	644	0.1882	0.4308	412.3	2.595	1.030	592
0.1757	0.6600	347.0	3.604	1.098	877	0.2433	0.4775	432.1	2.337	1.061	729
0.2090	0.6843	367.4	3.329	1.125	997	0.2983	0.5173	450.4	2.151	1.013	860
0.2723	0.7222	389.3	2.852	1.147	1112	0.3452	0.5336	456.1	1.940	1.154	935
0.3755	0.7500	404.0	2.227	1.234	1252	0.3891	0.5522	464.4	1.812	1.210	1007
0.4819	0.7716	412.0	1.820	1.390	1329	0.4596	0.5838	472.0	1.648	1.288	1066
0.5389	0.7806	415.0	1.658	1.510	1339	0.5022	0.5931	472.8	1.535	1.373	1079
0.6230	0.7899	416.7	1.457	1.776	1307	0.5303	0.6031	475.0	1.485	1.425	1089
0.7201	0.7900	418.0	1.266	2.399	1200	0.5344	0.6075	475.2	1.485	1.422	1086
0.8111	0.8105	418.5	1.153	3.212	938	0.5739	0.6176	475.9	1.407	1.517	1082
0.8653	0.8208	413.6	1.081	4.210	757	0.6193	0.6204	476.6	1.309	1.688	1060
0.9014	0.8355	409.0	1.046	5.222	589	0.6980	0.6425	470.4	1.191	1.979	949
0.9476	0.8674	404.8	1.003	7.843	323	0.7537	0.6624	466.3	1.127	2.272	846
0.9889	0.9459	385.0	1.017	14.34	133	0.7980	0.6823	458.5	1.079	2.557	724
						0.8647	0.7275	446.7	1.035	3.201	542
						0.9088	0.7723	434.2	1.017	3.859	400
						0.9592	0.8570	410.3	1.011	5.125	223

n-Heptane (1) + isobutanol (2) system — $p_1 = 361.3$ mm, $p_2 = 204.8$ mm
(and right) n-Heptane (1) + tert-butanol (2) system — $p_1 = 361.3$ mm, $p_2 = 564.1$ mm

In liquid	In vapour	P in mm	v_1	v_2	G^E	In liquln	In vapour	P in mm	v_1	v_2	G^E
0.0465	0.2713	265.7	4.314	0.9988	165	0.1066	0.1586	607.9	2.467	1.013	311
0.0860	0.3871	309.3	3.865	1.007	356	0.1486	0.2037	622.3	2.321	1.030	435
0.1358	0.4705	348.3	3.342	1.035	559	0.1888	0.2396	634.4	2.194	1.051	564
0.1954	0.5527	385.4	3.013	1.037	725	0.2296	0.2716	642.1	2.068	1.073	640
0.2508	0.5908	402.6	2.618	1.064	833	0.2674	0.2998	650.0	1.984	1.097	727
0.3200	0.6254	418.0	2.254	1.114	965	0.3123	0.3247	658.1	1.861	1.141	825
0.3841	0.6480	428.7	1.994	1.185	1070	0.3510	0.3483	662.0	1.786	1.174	891
0.4489	0.6647	436.1	1.779	1.282	1146	0.3999	0.3720	660.2	1.670	1.220	938
0.5108	0.6800	442.5	1.623	1.399	1192	0.4771	0.3887	655.9	1.453	1.354	975
0.5505	0.6852	445.2	1.525	1.507	1207	0.5238	0.4111	650.9	1.390	1.421	983
0.6052	0.6982	449.0	1.426	1.658	1200	0.5936	0.4424	641.9	1.303	1.556	975
0.6512	0.7054	451.0	1.345	1.840	1175	0.6389	0.4627	633.9	1.250	1.668	948
0.7136	0.7200	454.1	1.285	2.140	1131	0.6997	0.4918	620.6	1.190	1.857	889
0.8307	0.7519	447.1	1.114	3.165	825	0.7482	0.5273	604.2	1.161	2.006	832
0.9186	0.8101	434.6	1.055	4.900	519	0.8244	0.5728	574.4	1.091	2.476	668
0.9586	0.8794	412.3	1.042	5.811	326	0.8938	0.6472	530.2	1.052	3.127	481
						0.9439	0.7222	487.9	1.025	4.294	305
						0.9861	0.8190	442.2	1.011	10.140	126

The G^E is found to be positive throughout the concentration range for all the systems. It is a well established fact that the aliphatic alcohols undergo self-association through hydrogen bonding and these species break down on dilution with a non-polar solvent. The values of G^E are found to be in the order of $n > iso > sec > tert$. The maxima of G^E obtained are near about 1340, 1210,

TABLE 2 — VALUES OF SECOND VIRIAL COEFFICIENTS (B) AND MOLAR VOLUMES (VL) AT 75°

Compd	B (cm³ mol⁻¹)	VL (ml mol⁻¹)	Compd	B (cm³ mol⁻¹)	VL (ml mol⁻¹)
n-Heptane	—1094	157.42	sec-Butanol	—899	96.75
n-Butanol	—1068	96.72	tert-Butanol	—742	98.87
Isobutanol	—815	97.45			

TABLE 3 — COEFFICIENTS A_n AND STANDARD DEVIATIONS σ FOR RELATION BETWEEN G^E AND x_1 OF n-HEPTANE IN THE CASE OF ISOMERIC BUTANOLS AT 75°C

System	A_1	A_2	A_3	A_4	A_5	σ (Jmol⁻¹)
n-Butanol	5382.1	324.5	1769.8	—1499.9	—	35.15
Iso-butanol	4730.5	—832.2	1292.2	—922.0	—	22.62
sec-Butanol	4335.8	—602.3	—550.7	744.5	756.5	7.02
tert-Butanol	3958.5	—279.9	195.9	—1155.5	—1149.7	8.19

1090 and 985 J mol⁻¹ in the case *n*-, *iso*-, *sec*- and *tert*- butanols respectively. The above trend agrees well with Brown's observations[6] in case of binary mixtures of isomeric butanols with benzene. It is clear from above results that there is a pronounced effect on G^E due to branching to alkyl chain in isomeric butanols. At present it is not possible to interpret the data as we have yet to measure the enthalpy and entropy of mixing for all systems.

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Physico-chemical Studies in Non-aqueous Solvents: Part XIX—Viscosity Studies of Some 1:1 Electrolytes in Tetramethylurea

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Viscosities of some alkali metal salts and ammonium perchlorate have been measured in the concentration range 3.2-128.2 × 10⁻³ mol litre⁻¹ at 25° in tetramethylurea. The data have been analysed by the Jones-Dole equation. The viscosity B coefficients for all the electrolytes are positive and found to decrease with increasing size of the cation (except for NH^+_4 ion).

VISCOSITY measurements have been found to be useful in elucidating[1-3] the structures of electrolyte solutions. Except for a few tetraalkylammonium salts[4], viscosity and density studies of 1:1 electrolytes in tetramethylurea (TMU) have not been reported. In continuation of our earlier studies in TMU[5,6], we report here the results of our studies on viscosities of some 1:1 electrolytes in TMU at 25°.

Tetramethylurea (Fluka AG) was purified as reported[5] (b.p. = 76 -5°/12 mm, density = 0.9616 g cm⁻³, viscosity 1.404 × 10⁻² P and sp. cond. = 2-5 × 10⁻⁸ ohm⁻¹ cm⁻¹). The electrolytes used were prepared and/or purified by the methods already reported[7].

Viscosities were measured with a modified Ubbelohde capillary type viscometer[8] fitted with silica

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gel guard tubes in an electrically controlled water thermostat (± 0.01°). Four to six measurements were made for each concentration. The viscometer was calibrated with carbon tetrachloride (BDH AR, b.p. = 78.2°; η = 9.019 × 10⁻³ P; d = 1.584 g cm⁻³) and freshly distilled benzene (BDH) AR, m.p. = 5.51; η = 5.996 × 10⁻³ P; d = 0.8737 g cm⁻³).

Densities were determined using bicapillary pyconometer (capacity 9.5525 ml) which was calibrated with doubly distilled mercury (reproducibility ± 0.0001 g cm⁻³).

The viscosities of various solutions were calculated after applying kinetic energy correction[8].

Densities and viscosities of alkali metal and ammonium perchlorates, sodium and potassium thiocyanates and lithium and tetrabutylammonium bromides have been measured in the concentration range 3.2 - 128.9 × 10⁻³ mole litre⁻¹ at 25° in tetramethylurea. The data have been analysed by the Jones-Dole equation[9] (Eq. 1),

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

where η and η_0 are the viscosities of the solution and of pure solvent respectively and A and B are viscosity coefficients characteristic of the ions and the solvent. The viscocosity A and B coefficients have been computed by least squares method from the plots of $(\eta/\eta_0-1)/C^{1/2}$ versus $C^{1/2}$. The results are recorded in Table 1. The B value for tetrabutylammonium bromide obtained here agrees quite satisfactorily with the value reported by Barker and Caruso[4] (1.91 ± 0.05).

The viscosity A coefficients for NaSCN, $RbClO_4$ and NH_4ClO_4 have negative values. Although this has no physical meaning, similar observations have already been reported for tetraalkylammonium salts in TMU[4] and for some 1:1 electrolytes in other non-aqueous solvents[10-11]. This coefficient can also be calculated theoretically[2] from the limiting equivalent conductances and physical properties of the solvent. The values calculated for various electrolytes in TMU are also recorded in Table 1. However, theoretical A values for $LiClO_4$ and NH_4ClO_4 could not be calculated for the want of corresponding conductance data. The agreement between theoretical and experimental A values is satisfactory only in a few cases.

Table 1 shows that all the B values are positive

TABLE 1 — VALUES OF A AND B-COEFFICIENTS FOR SOME 1:1 ELECTROLYTES IN TMU AT 25°

Electrolyte	A		B
	(Expl)	(Theoret.)	(Expl)
LiBr	0.0267	0.0203	1.83
LiClO₄	0.0318	—	1.57
NaClO₄	0.0561	0.0202	1.48
Na SCN	—0.0065	0.0195	1.63
KClO₄	0.0727	0.0203	1.29
KSCN	0.0106	0.0185	1.35
RbClO₄	—0.0051	0.0200	1.26
CsClO₄	0.0189	0.0197	1.09
NH₄ClO₄	—0.0289	—	1.36