Thermochimica Acta, 15 (1976) 267–280

THERMODYNAMICS OF BINARY METHANOL SOLUTIONS

P. P. SINGH*, D. V. VERMA AND P. S. ARORA
Department of Chemistry and Biochemistry, Panjab Agricultural University, Ludhiana (India)
(Received 29 September 1975)

ABSTRACT

Excess enthalpies and change in volumes on mixing methanol with pyridine, β-picoline, N-N,-dimethylformamide and 1,4-dioxane have been determined at 303.15 K and 308.15 K and the same have been analysed for Barker's theory. It has been concluded that whereas the interaction of pyridine and β-picoline with methanol is attended by a decrease in self-association of the latter, that in methanol + 1,4-dioxane points to a strong associative interaction in methanol. It is further inferred that N,N-dimethylformamide is self-associated and it retains its associative form in its interaction with methanol. Self association energies in methanol and also in N,N-dimethylformamide have been calculated and a possible geometry of the complexes in methanol + pyridine, + β-picoline, + 1,4-dioxane and + N,N-dimethylformamide consistent with V^E and H^E data has been described. The pressure dependence of H^E has also been evaluated.

INTRODUCTION

In recent years there has been keen interest in the concept of the cooperative effect in the formation of multiple hydrogen bonded complexes. One early suggestion of this effect was made by Frank and Wen[1] in relation to their model for the structure of liquid water. It was consequently believed that the lower alcohols should also possess a degree of cooperativity in the formation of hydrogen bonded polymers. There has been, however, long controversy over alcohol association which still does not permit any absolute conclusions to be drawn regarding cooperative effects in alcohol self-association[2]. Further no thermodynamic data from alcohol association using enthalpies from models involving dimers and higher polymers directly support the qualitative conclusions[3] derived from frequency shifts in the infrared region for alcohol solutions in organic solvents. Nevertheless, thermodynamic data which clearly show cooperativity effects are of potential importance in the formation of improved theories of associated liquids. The present work describes the interaction

---

*Present address: Department of Chemistry, University of Lethbridge, Lethbridge, Alberta, Canada; and to whom all correspondence be sent.

of methanol with possible single site proton acceptors. Our choice of methanol was made by a suggestion of Liddel and Becker[4] that it contains both cyclic and open dimers in solution. On the other hand, Davies[6] maintains that association in amides in solution is limited to dimer formation.

EXPERIMENTAL

Pyridine and β-picoline were purified by standard procedures[7,8]. N,N-dimethylformamide, 1,4-dioxane and methanol were treated as suggested by Vogel[9]. (All reagents were of analytical grade BDH or Fluka.) The purities of the final samples were checked by density determinations at 303.15±0.01 K which agreed to within 0.00005 g cm^{-3} with those in the literature[10–14]. Sodium dried methanol was used in the present investigations.

Heats of mixing measurements were made in an adiabatic calorimeter described earlier[15]. Excess volumes were determined dilatometrically[16] adopting a slightly modified experimental procedure. It was observed that on mixing the components in the dilatometer, there was always some liquid column in the dilatometer capillary. To ensure that this liquid had the uniform bulk composition, the dilatometer was worked up as usual[16] and then placed in iced water at ≈ 283 K. This caused the liquid in the capillary to be sucked in. Care was, however, always taken that the capillary was not completely drained off the liquid. This was achieved by quickly dipping the dilatometer in the water thermostat. The cooling and warming process was repeated four or five times and the dilatometer finally adjusted in the water thermostat.

RESULTS

The excess enthalpies and change in volumes on mixing data at 303.15 K and 308.15 K are reported in Table 1. The H^E and V^E data, respectively, were fitted to the expression:

$$H^E/x_1(1-x_1) = \sum_{n=0}^{n=2} [(2x_1-1)^n H_n] \tag{1}$$

$$V^E/x_1(1-x_1) = \sum_{n=0}^{n=2} [(2x_1-1)^n A_n] \tag{2}$$

where x_1 is the mole fraction of component 1. The parameters H_n and A_n, evaluated by fitting $H^E/x_1(1-x_1)$ or $V^E/x_1(1-x_1)$ to expressions 1 and 2 by the method of least squares, together with the standard deviations $\sigma(H^E)$ and $\sigma(V^E)$ are recorded in Table 2.

TABLE 1

MEASURED V^E AND H^E AT 303.15 K AND 308.15 K FOR THE VARIOUS MIXTURES AND COMPARISON OF H^E VALUES AT 303.15 K CALCULATED ACCORDING TO BARKER'S THEORY WITH VALUES INTERPOLATED FROM THE MEASURED VALUES AT THREE MOLE FRACTIONS OF METHANOL (x_1)

x_1	V^E (*ml mol*$^{-1}$)	H^E (*J mol*$^{-1}$)	
		Exptl.	*Barker*
Methanol+pyridine at 303.15 K			
0.0705		−98.02	
0.1068		−161.34	
0.1208	−0.170		
0.1463		−247.80	
0.1959	−0.264		
0.2149	−0.285		
0.2204		−406.98	
0.2600		−480.12	
0.2847		−535.05	
0.2998	−0.374		
(0.3000)		(−580.0)	(−558.66)
0.3048	−0.380		
0.3202	−0.393		
0.3238		−622.82	
0.3670		−698.02	
0.3870		−732.68	
0.4415	−0.475		
0.4802		−827.55	
(0.5000)		(−840)	(−808.28), $(\partial H^E/\partial P)_T = -0.049$ J atm^{-1}
0.5600		−851.62	
0.5902	−0.490		
0.6150	−0.480		
0.6402		−802.17	
0.6835	−0.448		
(0.7000)		(−720)	(−740.12)
0.7188		−697.98	
0.7507	−0.390		
0.7804		−582.24	
0.8042	−0.336		
0.8563		−399.21	
0.9050	−0.185		
At 308.15 K			
0.0950	−0.131		
0.1250		−186.39	
0.1678	−0.230		
0.1965		−346.05	
0.2147	−0.285		
0.2260		−407.41	
0.2702		−502.63	

(*Table continued on p. 270*)

TABLE 1 (*continued*)

x_1	V^E (*ml mol*$^{-1}$)	H^E (*J mol*$^{-1}$)	
		Exptl.	*Barker*
At 308.15 K			
0.3119	−0.389		
0.3349		−619.89	
0.3655		−673.47	
0.3928	−0.436		
0.4220		−743.86	
0.5228		−808.28	
0.5548	−0.500		
0.5988		−785.60	
0.6397		−752.97	
0.6850	−0.459		
0.7050		−665.08	
0.7550	−0.402		
0.7649		−560.00	
0.8242		−434.15	
0.8615		−340.98	
Methanol + β-picoline 303.15 K			
0.0762		−250.04	
0.0980	−0.212		
0.1068	−0.232		
0.1270	−0.300		
0.1362		−458.53	
0.1850		−620.01	
0.1894	−0.406		
0.2267	−0.460		
0.2410		−798.68	
0.2804	−0.532		
0.2832		−903.91	
(0.3000)		−940	(−820.98)
0.3350		−1024.98	
0.3567	−0.598		
0.3994	−0.623		
0.4504		−1190.02	
0.4671	−0.645		
(0.5000)		(−1200)	−1074.67, $(\partial H^E/\partial P)_T = -0.068$ J atm^{-1}
0.5204	−0.650		
0.5400		−1180.05	
0.5952		−1122.88	
0.6149		−1090.00	
0.6207	−0.613		
0.6700		−983.20	
0.6708	−0.570		
(0.7000)		(−880)	(−991.50)
0.7452		−802.05	
0.7570	−0.475		
0.7987		−640.00	
0.8209	−0.371		
0.8300		−530.01	

TAPLE 1 (*continued*)

x_1	V^E (*ml mol*$^{-1}$)	H^E (*J mol*$^{-1}$)	
		Exptl.	*Barker*
Methanol + β-picoline 303.15 K			
0.8679	−0.288		
0.9208	−0.180		
At 308.15 K			
0.0905		−216.89	
0.1206	−0.230		
0.1504		−398.86	
0.1897	−0.345		
0.2068	−0.371		
0.2150		−580.03	
0.2570	−0.445		
0.2844		−780.56	
0.2880	−0.483		
0.3044		−840.66	
0.3182	−0.520		
0.3495		−925.64	
0.3612	−0.562		
0.3768		−982.03	
0.4102	−0.598		
0.4250		−1038.90	
0.4650	−0.625		
0.4852	−0.630		
0.5348		−1080.15	
0.5804		−1060.02	
0.5950	−0.610		
0.6130		−1019.53	
0.6398	−0.580		
0.6722		−918.01	
0.7143	−0.509		
0.7208		−796.98	
0.7300	−0.490		
0.7815		−630.15	
0.8300		−490.05	
0.8808	−0.250		
Methanol + N,N-dimethyl formamide 303.15 K			
0.0678		−18.05	
0.1162		−32.87	
0.1468	−0.130		
0.1805	−0.165		
0.1868		−57.67	
0.2567	−0.241		
0.2600		−81.52	
0.2751	−0.261		
(0.3000)		(−85)	(−92.63)
0.3050		−90.98	

(*Table continued on p. 272*)

TABLE 1 (*continued*)

x_1	V^E (*ml mol*$^{-1}$)	H^E (*J mol*$^{-1}$)	
		Exptl.	*Barker*
Methanol + N,N-dimethyl formamide 303.15 K			
0.3480	−0.324		
0.3549		−101.68	
0.3952	−0.364		
0.4150		−110.53	
0.4567	−0.402		
0.4670		−118.04	
0.4950	−0.425		
(0.5000)		(−117)	−108.69, $(\partial H^E/\partial P)_T = -0.044$ J atm^{-1}
0.5500		−111.68	
0.5655	−0.445		
0.6052		−108.12	
0.6250	−0.443		
0.6704	−0.440		
0.6750		−87.88	
(0.7000)		(−80)	(−80.00)
0.7100		−78.11	
0.7340	−0.415		
0.7950	−0.355		
0.8204		−45.08	
0.8230	−0.333		
0.8748		−28.15	
0.8952	−0.230		
At 308.15 K			
0.0809		−15.38	
0.1463		−34.86	
0.1762	−0.168		
0.2150	−0.201		
0.2587		−71.75	
0.2708	−0.252		
0.3047		−86.20	
0.3389	−0.309		
0.3809		−101.50	
0.4250	−0.371	−114.90	
0.4400	−0.383		
0.5211	−0.420		
0.5368		−118.02	
0.5620		−110.60	
0.5800	−0.431		
0.6200		−95.04	
0.6702	−0.423		
0.7397	−0.392		
0.7517		−62.50	
0.7918	−0.351		
0.8067		−44.11	
0.9112	−0.188		

TABLE 1 (*continued*)

x_1	V^E ($ml\ mol^{-1}$)	H^E ($J\ mol^{-1}$)	
		Exptl.	*Barker*
Methanol + 1,4-dioxane 303.15 K			
0.0569		172.60	
0.1162	−0.110		
0.1308		406.45	
0.1950	−0.184		
0.2068		635.14	
0.2280	−0.213		
0.2612		776.23	
(0.3000)		(880)	(825.18)
0.3150		890.32	
0.3568	−0.313		
0.3950		1000.02	
0.4319	−0.355		
0.4655		1040.68	
(0.5000)		(1040)	(968.71), $(\partial H^E/\partial P)_T = -0.039$ J atm^{-1}
0.5102		1038.98	
0.5120	−0.382		
0.5550		1010.05	
0.5608	−0.387		
0.5998		960.03	
0.6248	−0.381		
0.6430		885.67	
0.6664	−0.376		
(0.7000)		(740)	(739.85)
0.7080		760.02	
0.7232	−0.350		
0.7580		630.57	
0.7930		536.83	
0.8097	−0.281		
0.8564		362.78	
0.8850	−0.189		
At 308.15 K			
0.0760	−0.058		
0.0950		337.43	
0.1164		413.36	
0.1349	−0.100		
0.1806		620.38	
0.2107	−0.154		
0.2302		763.36	
0.2750	−0.195		
0.2800		886.27	
0.3048	−0.210		
0.3354		994.19	
0.3868		1064.38	
0.4220		1094.86	

(*Table continued on p. 274*)

TABLE 1 (*continued*)

x_1	V^E (*ml mol*$^{-1}$)	H^E (*J mol*$^{-1}$)	
		Exptl.	*Barker*
At 308.15 K			
0.4250	−0.263		
0.4846	−0.276		
0.5001	−0.279		
0.5048			
0.5548		1077.78	
0.5600	−0.281		
0.6272		984.19	
0.6302	−0.273		
0.6387		964.37	
0.7101	−0.247		
0.7150		802.95	
0.7900	−0.202		
0.7948		590.04	
0.8446		443.65	
0.9107	−0.100		

TABLE 2

PARAMETERS OF EQS (1) AND (2) ALONG WITH THE STANDARD DEVIATIONS $\sigma(V^E)$, $\sigma(H^E)$ AND THE INTERACTION ENERGIES U_1, U_2 AND U_3 FOR THE VARIOUS MIXTURES

	T(K)	A_0	A_1	A_2	H_0
Methanol + pyridine	303.15	−1.96	−0.3542	0.1667	−3360.04
	308.15	−1.96	−0.4501	0.1001	−3200.11
Methanol + β-picoline	303.15	−2.60	−0.067	0.251	−4778.50
	308.15	−2.52	−0.148	0.4708	−4358.80
Methanol + N,N-dimethyl formamide	303.15	−1.701	−0.8036	0.2007	−466.80
	308.15	−1.640	−0.7950	−0.0390	−466.80
Methanol + 1,4-dioxane	303.15	−1.516	−0.498	0.1233	4159.98
	308.15	−1.120	−0.2506	0.1321	4439.98

DISCUSSION

Heats of mixing for methanol + pyridine, + β-picoline, and + N,N-dimethylformamide are all negative; exothermicity varying in the order N,N-dimethylformamide < pyridine < β-picoline. The results, however, indicate endothermic mixing 1,4-dioxane + methanol. Further, whereas $\partial H^E/\partial T \approx 0$ for methanol + N,N-dimethylformamide, it is positive for all other mixtures studied here. The H^E data coupled with $\partial H^E/\partial T$ thus indicate that all these mixtures are characterized by specific interactions between their components.

V^E data for all these mixtures are negative and the contraction in volume follows the order 1,4-dioxane < N,N-dimethylformamide < pyridine < β-picoline. Again $\partial V^E/\partial T \approx 0$ for methanol + pyridine but it is positive for all other mixtures. The excess volumes of mixing also allow the pressure dependence of the excess enthalpy to be calculated according to the equation

$$(\partial H^E/\partial P) = V^E - T^E(\partial V^E/\partial T)_P \tag{3}$$

and these values are included in Table 1. Except for methanol + pyridine, it is observed that an increase of pressure leads to an increase in the amount of heat evolved. The trend in the values of $(\partial H^E/\partial P)_T$ closely parallels that in C_P^E for methanol + 1,4-dioxane, + pyridine and + N,N-dimethylformamide only. We now examine our V^E data for molecular interactions.

It is well known that methanol is associated in the pure state; consequently, it would occupy more space as a monomer than as a polymer. The addition of pyridine as in methanol + pyridine would result in interaction between the N atom of pyridine with the hydroxyl hydrogen of the methanol which would thus cause contraction in volume. Such a scheme of the nature of interactions would require still more contraction in volume in methanol + β-picoline. The experimental V^E data supports this

	H_2	$\sigma(V^E)$ (ml mol^{-1})	$\sigma(H^E)$ (J mol^{-1})	U_1 (J mol^{-1})	U_2 (J mol^{-1})	U_3 (J mol^{-1})
898.87	1521.40	0.0019	2.34	25.20	−2152.3	−5645.4
702.00	1600.05	0.0013	2.12			
177.40	2000.30	0.0023	5.95	25.20	−2152.3	−6048.65
180.71	2349.98	0.0016	6.02			
48.02	332.30	0.0021	1.96	12.60	−2721.89	−3906.42
47.30	449.98	0.0020	0.92			
500.02	−1709.97	0.0019	2.57	252.03	−2646.28	−2167.43
538.41	−1450.02	0.0014	2.72			

conjecture. Similar interaction may also characterize methanol+N,N-dimethyl formamide and methanol+1,4-dioxane mixtures.

The exothermic mixing in methanol+pyridine, +β-picoline and +N,N-dimethylformamide may be explained if we suppose that the interaction of methanol with the various bases involves: (i) partial depolymerisation of methanol (i.e., a partial elongation of its O–H bonds), and (ii) hydrogen bond formation so that the energy released in step (ii) more than compensates the energy required for step (i). The endothermic mixing in methanol+1,4-dioxane may thus be taken to suggest that the energy available from process (ii) is insufficient to that required for process (i).

In an alternate attempt to understand the nature of interactions between the components of these mixtures, we examined our results for Barker's theory[17]. This generalized lattice model theory allows a molecule occupying r_A sites on a Z coordinated lattice to have $q^z_A = r_A Z - 2r_A + 2$ neighboring contact sites; each type having a definite interaction energy. It is supposed that methanol has contact points, Q, representing hydroxyl hydrogen (H), oxygen (O) and the hydrocarbon (I) parts of the surface of the molecule.

For methanol+pyridine, +β-picoline and +1,4-dioxane, the geometrical parameters for this model were, lattice $Z=4$, methanol molecule (A) $r_A=2$, $q^z_A=6$, $Q_{\mathrm{HA}}=1$, $Q_{\mathrm{OA}}=2$ and $Q_{\mathrm{RA}}=3$; for pyridine, β-picoline $r_S=3$, $q^z_s=10$, $Q_{\mathrm{NS}}=2$ and $Q_{\mathrm{R'S}}=8$; and for 1,4-dioxane $Q_{\mathrm{O'S}}=2$ and $Q_{\mathrm{R'S}}=8$. The values of r_A and r_S where chosen to give a roughly correct value for the ratio of the molar volumes of the components. The interactions considered were: (a) hydrogen bond of strength U_3 between the hydroxyl hydrogen (H) of methanol and the N atom (O atom for 1,4-dioxane) of pyridine or β-picoline, (b) self-association of strength U_2 between the methanol molecules and (c) a non-specific interaction of strength U_1 for all the remaining contacts. U^E_V (excess energy at constant volume) values were then calculated from

$$U^E_V = -2RT[\{(X_O+X_N+X_{R'}+X_H)X_R+X_O(X_N+X_{R'})+X_{R'}(X_H+X_N)\}$$
$$\eta_1 \ln \eta_1+(X_N X_H \eta_3 \ln \eta_3)+(X_O X_H - x_A X'_O X'_H)\eta_2 \ln \eta_2] \tag{4}$$

where X_R, X_O, X_H, $X_{R'}$, (X_N or $X_{O'}$) were evaluated by solving the following simultaneous quadratic eqns (5)–(9) with certain assumed values for U_1, U_2 and U_3

$$X_R[X_R+\eta_1 X_O+\eta_1 X_H+\eta_1 X_N+\eta_1 X_{R'}] = Q_{\mathrm{RA}} x_A/2 \tag{5}$$

$$X_O[\eta_1 X_R+X_O+\eta_2 X_H+\eta_1 X_N+\eta_1 X_{R'}] = Q_{\mathrm{OA}} x_A/2 \tag{6}$$

$$X_H[\eta_1 X_R+\eta_2 X_O+X_H+\eta_3 X_N+\eta_1 X_{R'}] = Q_{\mathrm{HA}} x_A/2 \tag{7}$$

$$X_{R'}[\eta_1 X_R+\eta_1 X_O+\eta_1 X_H+\eta_1 X_N+X_{R'}] = Q_{\mathrm{R'S}} x_S/2 \tag{8}$$

$$X_N[\eta_1 X_R+\eta_1 X_O+\eta_3 X_H+X_N+\eta_1 X_{R'}] = Q_{\mathrm{NS}} x_S/2 \tag{9}$$

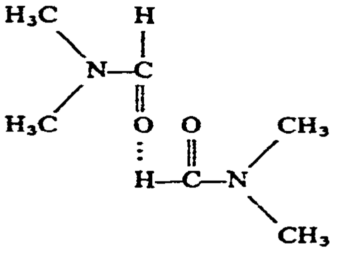
X'_H and X'_O are the solutions of the corresponding equations for pure methanol while $\eta_i = e^{-U_i RT}$ where U_i ($i=1$, 2 or 3) is the interaction energy per mole and R is the gas constant. U_V^E values at $x_1 = 0.3, 0.5$ and 0.7 could be converted (as is customary while testing a lattice theory) to measurements at constant pressure, i.e. H^E, using the relation

$$U_V^E = H^E - TV^E \alpha_m/(K_T)_m \tag{10}$$

where α_m, $(K_T)_m$ and V^E are the expansivity, isothermal compressibility and excess volume of the mixture, respectively. As the isothermal compressibility data for most of these compounds are not known, we have taken $U_V^E \approx H_P^E$.

Only those values of U_1, U_2 and U_3 were retained which reproduce as closely as possible the experimental H^E values. These values of the interaction energies are recorded in Table 2 and the calculated H^E values at various mole fractions of methanol are listed in Table 1. The thermodynamic consistency of these values of interaction energies could be checked from G^E measurements on these mixtures, work for which is in progress.

For methanol + N,N-dimethyl formamide, the interactions considered were: (i) a hydrogen bond of strength U_3 between the hydroxyl hydrogen and oxygen atom of methanol with the carbonyl oxygen and hydrogen atom of the formamide; (ii) self-association of strength U_2 between the methanol molecules and also between the formamide molecules, where the latter is assumed to have structure (A)



(A)

and, (iii) non-specific interaction of strength U_1 for all the remaining contacts. U_V^E values were then calculated from

$$\begin{aligned} U_V^E = & -2RT[\{X_R(X_O + X_H + X_{H'} + X_{O'} + X_{R'}) + X_{R'}(X'_O + X_H + X_O + X_{H'}) + \\ & + X_H X_{H'}\}\eta_1 \ln \eta_1 + (X_{O'} X_H + X_O X_{H'})\eta_3 \ln \eta_3 + (X_O X_H - x_A X'_O X'_H) \times \\ & \times \eta_2 \ln \eta_2 + (X_{O'} X_{H'} - x_B X'_{O'} X'_{H'})\eta_2 \ln \eta_2] \end{aligned} \tag{11}$$

where the various parameters were calculated by solving the following simultaneous quadratic equations for some assumed values of U_1, U_2 and U_3

$$X_R[X_R + \eta_1 X_O + \eta_1 X_H + \eta_1 X_{H'} + \eta_1 X_{O'} + \eta_1 X_{R'}] = Q_{RA} x_A/2 \tag{12}$$

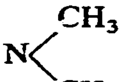
$$X_O[\eta_1 X_R + X_O + \eta_2 X_H + \eta_3 X_{H'} + \eta_1 X_{O'} + \eta_1 X_{R'}] = Q_{OA} x_A/2 \tag{13}$$

$$X_H[\eta_1 X_R + \eta_2 X_O + X_H + \eta_1 X_{H'} + \eta_3 X_{O'} + \eta_1 X_{R'}] = Q_{HA} x_A/2 \tag{14}$$

$$X_{H'}[\eta_1 X_R + \eta_3 X_O + \eta_1 X_H + X_{H'} + \eta_2 X_{O'} + \eta_1 X_{R'}] = Q_{H'B}x_B/2 \tag{15}$$

$$X_{O'}[\eta_1 X_R + \eta_1 X_O + \eta_3 X_H + \eta_2 X_{H'} + X_{O'} + \eta_1 X_{R'}] = Q_{O'B}x_B/2 \tag{16}$$

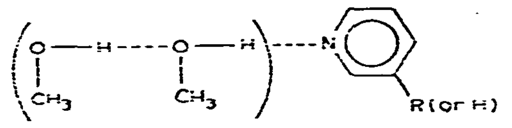
$$X_{R'}[\eta_1 X_R + \eta_1 X_O + \eta_1 X_H + \eta_1 X_{H'} + \eta_1 X_{O'} + X_{R'}] = Q_{R'B}x_B/2 \tag{17}$$

The quantities X_O, $X_{H'}$, $X_{O'}$, $X_{H'}$ are the solutions of the corresponding equations for pure methanol and N,N-dimethyl formamide. It is supposed that the N,N-dimethyl formamide had contact points representing carbonyl oxygen, O′, H atom (H′) and the  $\mathrm{N}\begin{smallmatrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{smallmatrix}$ (R′) parts of the surface of the molecule, so that $Q_{H'B} = 1$, $Q_{O'B} = 2$ and $Q_{R'B} = 7$.

Examination of Table 2 shows that Barker's theory describes H^E of mixtures of pyridine, β-picoline and N,N-dimethyl formamide well. However, the agreement is not so impressive for methanol + 1,4-dioxane; the failure in this case may be due to our assumption that this mixture contains 1:1 complexes only (because we have taken $Q_{HA} = 1$ for methanol).

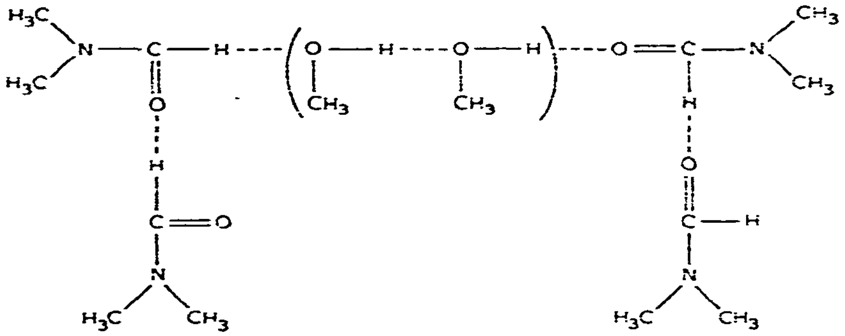
NATURE OF THE INTERACTIONS

We now make conjectures about the nature of interactions between the components of these mixtures. The U_3 interaction energies indicate that the hydrogen bonded interaction of pyridine, β-picoline, 1,4-dioxane and N,N-dimethyl formamide with methanol increases in the order β-picoline > pyridine > N,N-dimethyl formamide > 1,4-dioxane. On the other hand, the self-association energy (U_2) of methanol in its interaction with the various bases increases in the order N,N-dimethyl formamide ≈ 1,4-dioxane > pyridine = β-picoline. Thus the strong interaction of pyridine or β-picoline with methanol is attended by a decrease of self-association of the latter. This may be explained if we assume that the 1:1 complex in methanol + pyridine, + β-picoline has structure (B)



(B)

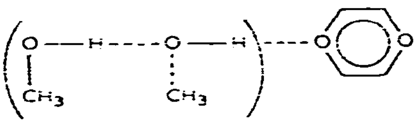
The strong hydrogen bonded interaction of pyridine or β-picoline with methanol tends to elongate the O–H bonds in the polymeric methanol and so weaken the self-association in the latter. Moreover, such a structure of the 1:1 complex of methanol + pyridine and + β-picoline would also explain the contraction in volume. Further, the large energy released in hydrogen bond formation in these mixtures more than compensates the energy required to elongate the O–H bonds in methanol which would also explain the exothermic mixing in them. The methanol + N,N-dimethyl formamide complex may be supposed to have structure (C)



(C)

Such a structure for the 1:1 complex in methanol + N,N-dimethyl formamide would require both the N,N-dimethyl formamide and methanol to have associative forms and the association energy of O′–H′ bond should be of the same magnitude as that of O–H bond in methanol. The U_2 association energies of N,N-dimethyl formamide are indeed equal to that of methanol in this mixture. Further in this structure the O–H bonds are not as stretched as they are in methanol + pyridine, which explains the large U_2 association energy in the former mixture compared to that of the latter.

The endothermic mixing in methanol + 1,4-dioxane may be explained if it is supposed that the hydrogen bonded interaction of 1,4-dioxane with methanol (as in (D))



(D)

releases less energy than is required to elongate the O–H bond in methanol. Such a conjecture would also require that methanol in methanol + 1,4-dioxane should be sufficiently strongly associated with U_2 association energy $< U_3$. The U_2 interaction energies of methanol in methanol + 1,4-dioxane and $U_2 < U_3$ does support this conjecture.

REFERENCES

1 H. S. Frank and W. Y. Wen, *Dics. Faraday Soc.*, 24 (1957) 133.
2 E. E. Tucker and E. D. Becker, *J. Phys. Chem.*, 77 (1973) 1783.
3 L. D. Bellamy and R. J. Pace, *Spectrochim. Acta*, 22 (1966) 525.
4 U. Liddel and E. D. Becker, *Spectrochim. Acta*, 10 (1957) 1957.

5 E. D. Becker, in "Hydrogen Bonding" edit. D. Hadzi and H. W. Thompson, Symposium Publications Division, Pergamon Press, New York, London, 1959.
6 M. Davies, in "Hydrogen Bonding" edit. D. Hadzi and H. W. Thompson, Symposium Publications Division, Pergamon Press, New York, London, 1959.
7 I. P. Alexander and R. H. Hugg, *J. Amer. Chem. Soc.*, 79 (1957) 4622.
8 D. G. Leis and B. C. Currans, *J. Amer. Chem. Soc.*, 67 (1945) 79.
9 A. Vogel, *Practical Organic Chemistry*, Longmans, Green and Co., London, 1968.
10 J. S. Bail, *J. Phys. Chem.*, 62 (1958) 858.
11 D. P. Biddiscombe, E. A. Coulson, R. Handley and E. F. G. Herington, *J. Chem. Soc.*, (1954) 1957.
12 B. E., Trav. Bur. Int. Et. Phys.-Chim. Bruxelles, J. Chim. Phys. 34 (1937) 693; quoted from J. Timmerman, Physico-Chemical Constants of Pure Organic Compounds, Elsevier, Amsterdam, 1950.
13 H. T. Briscoe and W. T. Rinehart, *J. Phys. Chem.*, 46 (1942) 387.
14 *Handbook of Chemistry and Physics*, Chemical Rubber Publishing Co., Cleveland, Ohio.
15 R. K. Nigam and B. S. Mahl, *J. Chem. Soc. Faraday I*, 68 (1972) 1508.
16 R. K. Nigam and P. P. Singh, *Trans. Faraday Soc.*, 65 (1969) 950.
17 J. A. Barker, *J. Chem. Phys.*, 30 (1952) 1526.