

An attempt has been made to substantiate this with the help of Grunberg's d' parameter¹¹ and the excess viscosity η^E . The values of these parameters are positive and change in magnitude up to 40% (v/v) of formic acid as expected for complex formation [$\eta^E = 0.033, 0.053, 0.060, \text{ and } 0.060; d' = 0.611, 0.494, 0.391 \text{ and } 0.382$ in 20, 40, 60 and 80% HCOOH respectively].

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Viscosities of Binary Liquid Mixtures of Formic Acid with Water, Methanol, Acetonitrile & Dimethylformamide

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The excess viscosity (η^E), molar free energy of activation of flow (g^{*E}), the interaction strength term (d') of Grunberg and Nissan equation and the interaction energy term (W_{visc}) of Katti and Chaudhri have been calculated from the densities and viscosities of the binary liquid mixtures of formic acid with water, methanol, acetonitrile and dimethylformamide at 30°C. It is observed that non-specific dipolar interactions are only present in formic acid + methanol and formic acid + acetonitrile mixtures while strong specific interactions are present in formic acid + dimethylformamide and formic acid + water mixtures. These specific interactions are attributed to the formation of molecular complexes (3:1 and 1:1 respectively) between the components.

EVENTHOUGH attempts have been made to study the molecular interactions in binary liquid mixtures containing formic acid, through the

measurement of excess thermodynamic functions, not many reports¹ are there using the viscosity data. The present note deals with the study of these interactions at 30°C in the title binary liquid mixtures in terms of excess viscosity (η^E), excess molar free energy of activation of flow (g^{*E}), the interaction strength factor of Grunberg and Nissan² (d') and interaction energy term (W_{visc}) of Katti and Chaudhri³.

The liquids were purified by the standard procedures⁴ and the measured densities and viscosities are in good agreement with the literature values^{5,6}. The literature values⁷ of density (0.9957 g/ml) and viscosity (0.8007 cp) at 30°C of water were used in the calculations.

Mixtures of known compositions were prepared by weight and the viscosities determined by the relative method of Ostwald. Densities were measured with a pycnometer of 25 ml capacity.

The values of η , η^E , g^{*E} , d' and W_{visc} calculated from the viscosity data are presented in Table 1.

The viscosities of the mixtures varied non-linearly with composition indicating a non-ideal behaviour. The variations of η^E and g^{*E} with mol fraction of formic acid indicates a maximum in both the parameters in the case of formic acid + water (FA+W) and formic acid + dimethylformamide (FA+DMF) systems. The positive values of η^E with a marked maximum indicates strong unlike interactions resulting in the formation of a complex⁸. The composition of the complexes is 3:1 (FA:DMF) and 1:1 (FA:W) respectively. The higher positive η^E values for FA + DMF mixture suggests that the complex formed in this system is more stable than that between FA and W. Similar behaviour was reported by Solimo and coworkers in the case of binary liquid mixtures of propionic acid⁹ with aniline, pyridine and dimethylaniline.

The negative values of η^E in the case of formic acid + methanol (FA + M) and formic acid + acetonitrile (FA + AN) suggest that dispersion forces are dominant in these systems. Similar trend was reported by Katz *et al.*¹⁰ in the case of binary liquid mixtures of aniline with toluene and butanol.

The FA + M system is having greater g^{*E} values than the FA + AN system (Table 1). This situation is reverse of that observed in the case of η^E values. This could be attributed to the influence of viscosity (η) and molar volume (V) simultaneously¹¹. The non-zero value of d' indicates the non-ideal behaviour of the mixtures. The trend in d' values is almost the same as that in η^E values.

The large negative values of W_{visc} in the case of FA + M and FA + AN systems show an appreciable dipole-dipole interaction between the components, while the positive values in FA + W and FA + DMF systems show weak interactions. Dimethylformamide, methanol and water are associated in the pure state while acetonitrile is not. Addition of formic acid to these liquids is expected to cause similar changes. However methanol-formic acid mixture exhibits different behaviour.

TABLE 1 — SOME PHYSICAL PROPERTIES OF BINARY LIQUID MIXTURES OF FORMIC ACID WITH WATER, DIMETHYL FORMAMIDE, METHANOL AND ACETONITRILE

Mol fr. of HCOOH x_1	η (cp)	η^E (cp)	g^*E (cal mol ⁻¹)	d'	W_{v180}
HCOOH(FA) + H ₂ O(W)					
0.0000	0.801	—	—	—	—
0.0501	0.849	0.019	26.8	0.656	563.6
0.1061	0.897	0.037	51.4	0.604	542.6
0.1690	0.950	0.053	72.1	0.576	513.2
0.2404	0.994	0.057	86.4	0.480	473.1
0.3219	1.062	0.079	103.2	0.507	472.8
0.4159	1.156	0.120	122.4	0.596	503.7
0.5255	1.159	0.060	96.9	0.355	388.6
0.6550	1.234	0.062	89.7	0.362	396.9
0.8103	1.288	0.028	55.5	0.270	361.1
1.0000	1.434	—	—	—	—
HCOOH(FA)+CH ₃ OH(M)					
0.0000	0.545	—	—	—	—
0.0714	0.573	-0.031	-11.5	-0.226	-133.7
0.1463	0.609	-0.056	-17.5	-0.185	-140.3
0.2264	0.641	-0.100	-31.2	-0.263	-178.3
0.3137	0.658	-0.146	-64.5	-0.465	-299.5
0.4031	0.677	-0.201	-96.6	-0.642	-401.4
0.5060	0.691	-0.273	-140.9	-0.922	-563.5
0.6149	0.750	-0.304	-149.6	-1.048	-680.4
0.7328	0.867	-0.285	-128.1	-1.089	-653.9
0.8604	1.062	-0.196	-76.7	-1.067	-638.7
1.0000	1.434	—	—	—	—
HCOOH(FA)+CH ₃ CN(AN)					
0.0000	0.353	—	—	—	—
0.0912	0.386	-0.066	-20.4	-0.470	-245.8
0.1824	0.422	-0.128	-42.0	-0.519	-281.7
0.2772	0.468	-0.185	-56.7	-0.530	-283.0
0.3728	0.523	-0.232	-68.9	-0.548	-294.8
0.4721	0.597	-0.340	-72.2	-0.544	-289.6
0.5735	0.691	-0.282	-70.2	-0.526	-287.1
0.6751	0.801	-0.281	-67.1	-0.551	-285.8
0.7806	0.962	-0.234	-47.8	-0.521	-279.3
0.8891	1.166	-0.149	-26.8	-0.363	-271.8
1.0000	1.434	—	—	—	—
HCOOH(FA)+(CH ₃) ₂ NCO.H(DMF)					
0.0000	0.758	—	—	—	—
0.1513	0.848	-0.012	42.4	0.125	330.5
0.2841	0.986	0.036	90.2	0.402	443.4
0.4038	1.164	0.133	137.6	0.711	571.4
0.5138	1.318	0.213	173.2	0.904	693.5
0.6144	1.445	0.272	223.2	1.072	942.0
0.7043	1.532	0.298	187.4	1.223	900.0
0.7869	1.584	0.295	170.8	1.406	1018.4
0.8657	1.576	0.233	129.4	1.546	1112.9
0.9348	1.546	0.156	81.7	1.916	1341.0
1.0000	1.434	—	—	—	—

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Cryoscopic Studies in Molten Salts : Dissociation of Some Alkali Isopolymolybdates & Some Related Molybdenum(VI) Compounds in Molten Potassium Dichromate & Potassium Nitrate

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The dissociation of the solutes, viz. M_2MoO_4 , $M_2Mo_3O_{14}$, $M_2Mo_4O_{18}$, $M_2Mo_5O_{18}$ (M=Rb or Cs), $Na_2CrO_4 \cdot MoO_3$, $K_2CrO_4 \cdot 2MoO_3$, $Cr_2Mo_3O_{12}$ and V_2MoO_8 in molten $K_2Cr_2O_7$ and KNO_3 as solvents has been studied employing cryoscopic method. The values of number of foreign ions (ν) show that all the solutes, except V_2MoO_8 , are either simply dissociated in the melt, or, in some cases after dissociation undergo rearrangement to heteropolyions of the type $(CrMo_2O_{10})^{2-}$. The solute V_2MoO_8 dissolves without any apparent dissociation. An agreement between the experimental and calculated values of activity (a) based on the Temkin and random mixing models and that of Vant Hoff's equation support the proposed simple dissociation scheme for $K_2Cr_2O_7$ - Cs_2MoO_4 system.

It is well known that the freezing point of a pure solvent is lowered provided the foreign ions or species present are different from those of the dissociation products of the solvent. The factor, ν , gives only the number of such foreign species formed, rather than the effects of the forces they exert, i.e. it expresses a molecular property of the solute. The ν -value is evaluated by measuring the freezing point depression (ΔT) of solvents induced by solutes, in very dilute solutions, where Raoult-Vant Hoff's law (1) of freezing point depression is obeyed.

$$\Delta T = T_1 - T = \nu \cdot x_2 \cdot \left[\frac{R T_1^2}{L_1} \right] \quad \dots(1)$$

In Eq. (1) T_1 and T are the crystallisation temperatures in K of the pure solvent and the mixture, respectively; L_1 is the melt enthalpy (in cal/mol) of the solvent; x_2 is the mole fraction of the solute; and R is the ideal gas constant (1.986 cal. deg.⁻¹ mol⁻¹).