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Physico-Chemical Studies on Furyl Acrylic Acid

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Furyl acrylic acid (FAA) was chatacterized by IR and NMR. The density of FAA was determined from partial specific volume at 31°C. The refractive index and molar heat of fusion were determined from methanol and benzene solutions, respectively at 31°C.

INTRODUCTION

It is well known that furyl acrylic acid (FAA) and its esters are useful in the preparation of plastic materials[1–4], synthetic rubber like material[5], and synthetic drying oils[6,7]. The present work describes the synthesis, characterization and determination of density, refractive index (RI) and molar heat of fusion at 31°C.

EXPERIMENTAL

Furyl acrylic acid (FAA) was prepared from furfural, malonic acid and pyridine as catalyst.[1–3,8] FAA was purified from hot water and benzene till m.pt. 139–140°C obtained. IR spectrum was scanned on a Shimadzu DR–1 and NMR spectrum was scanned on a XL 100A spectrometer operating at 100.1 MHz using DMSO–d_6 as solvent and TMS, as an internal reference.

A series of FAA–methanol solutions were prepared at 31°C (Table 1). The density and specific volume of each solution were determined using specific gravity bottle and RI was determined on Abbe refractometer at 31°C.

A series of saturated FAA solutions in benzene were prepared at a specified temperature (Table 1). The solubility of FAA at a specified temperature was determined by transferring a known volume (25 ml) of saturated solution into a preweighed 50 ml beaker and benzene was evaporated to dryness by blowing hot air till constant weight and the weight of the dry residue was determined. Similarly at each temperature the solubility determination was carried out at least three times and the mean values reported. The amount of benzene in a saturated solution was determined by determining the weight of the 25 ml solution in a stoppered conical flask and weight of the solute in 25 ml solution. Finally the moles of benzene and FAA were determined in litre of saturated solution.

RESULTS AND DISCUSSION

The characteristic IR frequencies (cm^{-1}) of FAA are: 3110–2300 (OH), 1700 (C=O, ν_{asym}), 1620 (C=C vinyl stretch), 1410 (C=O, ν_s), 1304 (C—O and OH) and 1222 (C—O—C) besides normal modes of vibrations.

NMR spectrum of FAA revealed the following signals (δ): 12.37 (s, OH), 7.84–7.86 (d, 1H of —CH=CH—, J = 2), 7.53–7.37 (d, 1 ArH, J = 16), 6.97–6.94 (d, 1H of —CH=CH, J = 3), 6.62–6.68 (q, 1 ArH, J = 6) and 6.29–6.14 (s, 1 ArH, J = 15).

The results of the density and RI measurements of FAA–methanol solutions at 31°C are reported in Table 1. The density of the solute ρ_2 is inversely related with the partial specific volume $\overline{V}_2$. The density of the solution ρ_{12} is

$$\frac{1}{\rho_{12}} = \frac{g_1}{\rho_1} + \frac{g_2}{\rho_2} \tag{1}$$

Where symbols have their own significance.

Thus upon rearranging

$$\overline{V}_2 = \frac{1}{\rho_2} = \frac{1}{g_2} \frac{(\rho_1 - g_1\rho_{12})}{\rho_1\rho_{12}} \tag{2}$$

The value of ρ_2 of each solution was calculated according to eqn. (2). From the least square analysis the density of FAA is found to be 1.191 g ml^{-1} at 31°C.

RI is a property of the material and is extremely useful in chemical analyses and process control and molar refraction is of great importance in the calculation of dipole moment. The molar refractions of pure solvent and solutions can be determined according to Lorenz and Lorenz[9]. From density and RI data on FAA–methanol solutions at 31°C, the molar refraction of FAA at a specified composition was calculated according to Lorenz and Lorenz[9] equations (Table 1) and RI of FAA. The intrinsic RI was determined by plotting RI of solution against mole fraction X_2 and extrapolating to zero concentration. Thus, the RI obtained from least square analysis is found to be 1.719.

The molar heat of fusion, ΔH_f and melting temperature, Tm of a substance can be determined from the solubility measurements at different temperatures[10]. The variation of the solubility with temperature[10] is given by

$$\left(\frac{\partial \ln N_2}{\partial_T}\right)_P = \frac{\Delta H_f}{RT^2} \tag{3}$$

where symbols have their own significance. The eqn. (3) is based on two assumptions: the solution behaves idealy and the solute which separates from solutions is always pure solute and not a solid solution. If the heat of fusion is independent of temperature, then

TABLE 1
DENSITY AND RI DATA ON FAA-METHANOL SOLUTIONS AT 31°C

Wt. fr. of MeOH g_1	Wt. fr. of FAA g_1	Mol. fr. X_1	Mol. fr. X_2	Density of solution ρ_{12} g/ml	RI of solution	ρ_2 g/ml	$(M_{R_D})_2$	RI FAA
0.9459	0.0541	0.9870	0.0130	0.7999	1.3580	1.1184	44.85	1.6988
0.9276	0.0724	0.9822	0.0178	0.8060	1.3625	1.1650	44.90	1.6997
0.8917	0.1083	0.9726	0.0274	0.8160	1.3695	1.1700	44.08	1.6832
0.8183	0.1817	0.9510	0.0490	0.8449	1.3855	1.2636	42.04	1.6434
0.7821	0.2179	0.9394	0.0606	0.8547	1.3915	1.2372	41.72	1.6372

ρ_1 = 0.787 g/ml, RI = 1.3475 and $(M_{R_D})_1$ = 8.69

$$\ln N_2 = \frac{\Delta H_f}{R}\left(\frac{1}{T_m} - \frac{1}{T}\right) \quad (4)$$

According to eqn. (4), if log N_2 is plotted against $\frac{1}{T}$, a straight line is obtained. From the solubility measurements at different temperatures, the values of ΔH_f and Tm were determined from the slope and intercept, respectively. The least square values of ΔH_f and Tm are found to be 10.75 Kcal/mol and 138°C, respectively. Thus the value of Tm obtained from the solubility measurement is in good agreement with the reported m.pt. 139–140°C. The slight discrepancy in Tm might be due to the variation of experimental temperature (± 1°C). The appropriate values of ΔH_f and Tm can be obtained for the ideal behaviour and it is only possible when the structures of the binary components are nearly the same. By selecting the analogue structures of the solvent and solute for any system precise values of ΔH_f and Tm can be determined from the solubility measurements.

TABLE 2
SOLUBILITY DATA ON FAA-BENZENE SYSTEM

Temp. °C	30	33	38	41	45
Solubility of FAA, N_2	0.0105	0.0125	0.0173	0.0198	0.0243

ΔH_f = 10.75 kcal/mol and Tm = 138°C

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