

Studies of Acoustical Properties of Methyl Salicylate in Different Solvents

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Acoustical properties in different compositions of methyl salicylate-dioxane (MS-DO), methyl salicylate-methanol (MS-MeOH) and methyl salicylate-benzene (MS-BN) were studied at 30°C using a single crystal multifrequency interferometer operating at 3 MHz. Various acoustical and thermodynamic parameters like isentropic compressibility (K_s), specific impedance (Z), intermolecular free path (L_f), molar sound velocity (R), relaxation strength (r), the van der Waals constant (b), internal pressure (π), relaxation time (τ), classical adsorption coefficient ($(\alpha/f^2)_{Cl}$), molecular diameter (d_M), surface tension (σ), excess volume (V^E), excess viscosity (η^E), excess sound velocity (U^E), excess Gibbs free energy of activation of flow (ΔG^E) etc. were evaluated using experimental data of sound velocity (U), density (ρ) and viscosity (η) at 30°C. The results are interpreted in terms of interactions taking place in solutions.

INTRODUCTION

Knowledge of thermodynamic and acoustical properties is of great significance in studying the physico-chemical behaviour and molecular interactions in a variety of liquid mixtures^{1–6}. In continuation of our previous work^{7, 8}, an attempt is made to evaluate the acoustical properties in different compositions of methyl salicylate-dioxane (MS-DO), methyl salicylate-methanol (MS-MeOH) and methyl salicylate-benzene (MS-BN) systems at 30°C.

EXPERIMENTAL

Solvents used for the study were purified⁹ and redistilled prior to use. The purity of solvents was checked by gas-liquid chromatography. The estimated purity of all the solvents was better than 99.5%. Solutions of different compositions of MS were prepared by mixing v/v with solvents like MeOH, dioxane and benzene.

Ultrasonic velocity (U), viscosity (η) and density (ρ) of these solutions were measured at $30 \pm 0.1^\circ\text{C}$ using M-82 multifrequency interferometer operating at 3 MHz, suspended level Ubbelohde viscometer and by pycnometer with an accuracy of $\pm 0.06\%$, $\pm 0.01\%$ and 0.0001 g mL^{-1} , respectively.

RESULTS AND DISCUSSION

Using ultrasonic velocity, density and viscosity data (Table-1), various acoustical properties like isentropic compressibility (K_s), specific acoustic impedance (Z), intermolecular free length (L_f), internal pressure (π), relaxation strength (r), molar sound velocity (R), molar compressibility (W), van der Waals constant (b), relaxation time (τ) and classical absorption coefficient ($(\alpha/f^2)_{Cl}$) have been calculated using equations reported earlier⁷. Some of these parameters are given in Table-2. Further, the correlation coefficients and correlation equations for different parameters with concentration are given in Table-3.

TABLE-1
VARIATION OF DENSITY (ρ), VELOCITY (U) AND VISCOSITY (η) WITH X_{MS} IN THE THREE BINARY SYSTEMS AT 30°C.

| X_{MS} | Density, ρ g/cm ³ | Velocity, $U \times 10^5$ cm/sec | Viscosity, η poise |
|----------|--------------------------------------|-------------------------------------|----------------------------|
| MS-DO | | | |
| 0.0000 | 1.0000 | 1.3288 | 0.0105 |
| 0.0700 | 1.0354 | 1.3322 | 0.0112 |
| 0.1427 | 1.0533 | 1.3419 | 0.0121 |
| 0.3077 | 1.0832 | 1.3469 | 0.0140 |
| 0.4997 | 1.1124 | 1.3616 | 0.0165 |
| 0.7272 | 1.1440 | 1.3740 | 0.0189 |
| 1.0000 | 1.1753 | 1.3980 | 0.0238 |
| MS-MeOH | | | |
| 0.0000 | 0.7970 | 1.1006 | 0.0056 |
| 0.0720 | 0.8699 | 1.1464 | 0.0063 |
| 0.1713 | 0.9494 | 1.1981 | 0.0096 |
| 0.3175 | 1.0280 | 1.2456 | 0.0114 |
| 0.5538 | 1.1038 | 1.3093 | 0.0158 |
| 0.7303 | 1.1405 | 1.3506 | 0.0192 |
| MS-BN | | | |
| 0.0000 | 0.8701 | 1.2740 | 0.0054 |
| 0.0706 | 0.8980 | 1.2806 | 0.0060 |
| 0.1476 | 0.9294 | 1.2900 | 0.0067 |
| 0.3159 | 0.9925 | 1.3044 | 0.0085 |
| 0.5096 | 1.0539 | 1.3236 | 0.0109 |
| 0.7348 | 1.1150 | 1.3584 | 0.0151 |

TABLE-2
 VARIATION OF K_s , Z , L_f , π , $(\alpha/f^2)_{cl}$ AND τ WITH X_{MS} IN ALL
 THE THREE SYSTEMS AT 30°C

| X_{MS} | K_s $\times 10^{11} \text{ cm}^2/\text{dyne}$ | Z $\times 10^{-5} \text{ g/cm}^2$ | L_f Å | π atmos | $(\alpha/f^2)_{cl}$ $\times 10^{11}$ | τ $\times 10^{12}$ |
|----------|--|--|---------------------|----------------|---|----------------------------|
| MS-DO | | | | | | |
| 1.0000 | 4.3534 | 1.6431 | 0.4013 | 430.5891 | 2.7257 | 1.3798 |
| 0.7272 | 4.6301 | 1.5719 | 0.4138 | 421.0361 | 2.3002 | 1.1643 |
| 0.4997 | 4.8490 | 1.5146 | 0.4235 | 434.9080 | 2.1112 | 1.0687 |
| 0.3077 | 5.0887 | 1.4590 | 0.4338 | 447.6078 | 1.8752 | 0.9492 |
| 0.1427 | 5.2725 | 1.4134 | 0.4416 | 469.7914 | 1.6748 | 0.8478 |
| 0.0700 | 5.5228 | 1.4023 | 0.4450 | 490.8884 | 1.6078 | 0.8054 |
| 0.0000 | 5.5372 | 1.3591 | 0.4525 | 506.3174 | 1.5329 | 0.7759 |
| MS-MeOH | | | | | | |
| 1.0000 | 4.3534 | 1.6431 | 0.4058 | 430.5891 | 2.7257 | 1.3798 |
| 0.7303 | 4.8522 | 1.5221 | 0.4250 | 426.0659 | 2.4002 | 1.1822 |
| 0.5538 | 5.4084 | 1.4152 | 0.4421 | 431.5477 | 2.1036 | 1.0755 |
| 0.3175 | 6.2697 | 1.2805 | 0.4815 | 450.5112 | 1.8876 | 0.9555 |
| 0.1713 | 7.3378 | 1.1375 | 0.5210 | 540.8664 | 1.8458 | 0.9343 |
| 0.0720 | 8.7470 | 0.9973 | 0.5688 | 642.4577 | 1.4515 | 0.7347 |
| 0.0000 | 10.3582 | 0.8772 | 0.6190 | 1120.9770 | 1.5279 | 0.7734 |
| MS-BN | | | | | | |
| 1.0000 | 4.3534 | 1.6431 | 0.4058 | 430.5891 | 2.7257 | 1.3798 |
| 0.7348 | 4.8604 | 1.5146 | 0.4240 | 379.3701 | 1.9383 | 0.9811 |
| 0.5096 | 5.4161 | 1.3949 | 0.4476 | 359.6923 | 1.5621 | 0.7908 |
| 0.3159 | 5.9217 | 1.2946 | 0.4680 | 355.2329 | 1.3227 | 0.6695 |
| 0.1476 | 6.4657 | 1.1989 | 0.4890 | 360.8291 | 1.1326 | 0.5733 |
| 0.0706 | 6.7522 | 1.1550 | 0.4950 | 372.0320 | 1.1010 | 0.5523 |
| 0.0000 | 7.0810 | 1.1085 | 0.5118 | 385.0384 | 1.0146 | 0.5136 |

From Table-3, it is observed that except for some parameter in MS-MeOH systems, an excellent correlation between the parameters and concentrations are observed in other systems.

Surface tension (σ) and molecular diameters (d_M) for all the compositions of the systems were calculated by the following equations¹⁰ and are reported in Table-4.

$$d_M = (2^{1/6}(V\pi - RT))/(\pi N^{1/3}V^{2/3}) \quad (1)$$

$$\sigma = 6.3 \times 10^{-4} \rho U^{3/2} \quad (2)$$

where V is the molar volume, π the internal pressure and N the Avogadro's number; other symbols have their usual significance.

TABLE-3
THE CORRELATION COEFFICIENTS (γ) AND THE CORRELATION EQUATIONS FOR
SOME PARAMETERS IN THE THREE SYSTEMS AT 30°C

| Parameter γ | Correlation Coefficient (γ) | Correlation equation |
|--|--------------------------------------|------------------------------|
| MS-DO | | |
| $Z \times 10^5$ (g/cm ² sec) | 0.9995 | $Z - 272.5248C = 1.3754$ |
| $K_s \times 10^{-11}$ (cm ² /dyn) | 0.9986 | $K_s + 1.1C = 5.43$ |
| R | 0.9956 | $R - 2353.7530C = 4619.04$ |
| W | 0.9960 | $W - 1417.3490C = 2643.141$ |
| b | 0.9951 | $b - 43.4278C = 85.2873$ |
| r | 0.9907 | $r + 0.0609C = 0.3071$ |
| $L_f \text{ \AA}$ | 0.9990 | $L_f + 0.0481C = 0.4483$ |
| π | 0.9805 | $\pi + 80.6295C = 4.77.1458$ |
| MS-MeOH | | |
| $Z \times 10^5$ (g/cm ² sec) | 0.9995 | $Z - 778.7410C = 0.9888$ |
| $K_s \times 10^{-11}$ (cm ² /dyn) | 0.9986 | $K_s + 5.6C = 8.55$ |
| R | 0.9719 | $R - 4721.111C = 3185.657$ |
| W | 0.9722 | $W - 2811.115C = 1790.395$ |
| b | 0.9621 | $b - 83.2319C = 61.4126$ |
| r | 0.9930 | $r + 0.2900C = 0.4952$ |
| $L_f \text{ \AA}$ | 0.9657 | $L_f + 0.2086C = 0.5646$ |
| π | 0.8722 | $\pi + 30.4868C = 608.7485$ |
| MS-BN | | |
| $Z \times 10^5$ (g/cm ² sec) | 0.9998 | $Z - 539.7706C = 1.1197$ |
| $K_s \times 10^{-11}$ (cm ² /dyn) | 0.9974 | $K_s + 2.8C = 6.89$ |
| R | 0.9960 | $R - 2173.375C = 4772.558$ |
| W | 0.9963 | $W - 1373.087C = 2677.227$ |
| b | 0.9943 | $b - 39.3208C = 89.1539$ |
| r | 0.9887 | $r + 0.1198C = 0.3712$ |
| $L_f \text{ \AA}$ | 0.9993 | $L_f + 0.1086C = 0.5033$ |
| π | 0.9807 | $\pi + 32.4790C = 349.913$ |

The excess volume (V^E), excess viscosity (η^E), excess velocity (U^E), excess Gibb's free energy of activation of flow¹¹ (ΔG^E) and Grunberg and Nissan characteristic parameter¹² (d) were calculated from the following relations:

$$V^E = (M_1X_1 + M_2X_2)/\rho_{12} - (M_1X_1/\rho_1) - (M_2X_2/\rho_2) \quad (3)$$

$$\eta^E = \eta_{12} - X_1\eta_1 - X_2\eta_2 \quad (4)$$

$$U^E = U_{12} - X_1U_1 - X_2U_2 \quad (5)$$

$$\Delta G^E = RT\{\ln \eta_{12}V_{12} - X_1 \ln \eta_1V_1 - X_2 \ln \eta_2V_2\} \quad (6)$$

$$d = [\ln \eta_{12} - X_1 \ln \eta_1 - X_2 \ln \eta_2]/X_1X_2 \quad (7)$$

where ρ_{12} , ρ_1 and ρ_2 , η_{12} , η_1 and η_2 , U_{12} , U_1 and U_2 and V_{12} , V_1 and V_2 are the densities, viscosities, velocities and molar volumes of the mixture and of the pure components respectively; M_1 and M_2 are the molecular weights of the pure components; and X_1 and X_2 are the mole fractions of the pure components. V^E , η^E , U^E , ΔG^E and d are given in Table-4.

TABLE-4
VARIATION OF EXCESS VOLUME, EXCESS VISCOSITY, EXCESS VELOCITY, EXCESS GIBBS FREE ENERGY OF ACTIVATION OF FLOW, GRUNBERG AND NISSAN CHARACTERISTIC PARAMETER, SURFACE TENSION AND MOLECULAR DIAMETER WITH X_{MS} IN ALL THE THREE SYSTEMS AT 30°C

| X_{MS} | V^E cm^3/mol | η^E $\times 10^4$ poise | U^E $\times 10^{-3}$ | ΔG^E J/mol | d | σ dyne/cm | d_M Å |
|----------|-----------------------------------|---------------------------------|---------------------------|-----------------------|--------|---------------------|------------|
| MS-DO | | | | | | | |
| 1.0000 | - | - | - | - | - | 38.7035 | 6.4199 |
| 0.7272 | 0.0859 | 12.927 | -5.1222 | 18.613 | -0.044 | 36.7068 | 6.2649 |
| 0.4997 | 0.1864 | 6.060 | -1.7792 | 169.715 | +0.180 | 35.2108 | 6.1073 |
| 0.3077 | 0.0614 | 6.001 | -3.1928 | 136.114 | +0.164 | 33.7328 | 5.9341 |
| 0.1427 | 0.0012 | 3.422 | -3.2252 | 81.337 | +0.173 | 32.6192 | 5.7415 |
| 0.0700 | -1.0779 | -2.382 | -1.6440 | 0.947 | +0.099 | 32.1884 | 5.5690 |
| 0.0000 | - | - | - | - | - | 31.2119 | 5.5311 |
| MS-MeOH | | | | | | | |
| 1.0000 | - | - | - | - | - | 38.7035 | 6.4199 |
| 0.7303 | -0.3412 | +8.1040 | 32.2980 | 796.771 | +0.999 | 35.1837 | 5.9464 |
| 0.5538 | -0.3050 | +5.2742 | 43.9998 | 980.590 | +0.965 | 32.9450 | 5.5465 |
| 0.3175 | -0.2507 | +2.6740 | 50.5755 | 1040.731 | +1.174 | 28.4709 | 4.9863 |
| 0.1713 | -0.0051 | +9.4882 | 46.5553 | 1025.915 | +2.016 | 24.8044 | 4.6403 |
| 0.0720 | +0.1588 | -5.6114 | 24.3872 | 204.463 | +0.205 | 21.2723 | 4.3857 |
| 0.0000 | - | - | - | - | - | 18.3334 | 4.2965 |
| MS-BN | | | | | | | |
| 1.0000 | - | - | - | - | - | 38.7035 | 6.4199 |
| 0.7348 | -0.0369 | -0.2909 | -6.7152 | -121.614 | -0.308 | 35.1687 | 6.2563 |
| 0.5096 | -0.0396 | -0.3235 | -13.5904 | -90.168 | -0.208 | 31.9724 | 6.0955 |
| 0.3159 | -0.0135 | -0.2381 | -8.7716 | -17.675 | -0.101 | 29.4569 | 5.9244 |
| 0.1476 | +0.1881 | -0.1323 | -2.3024 | -14.329 | -0.134 | 27.1286 | 5.7358 |
| 0.0706 | +0.2119 | -0.6412 | -2.6800 | -13.6707 | -0.157 | 26.0322 | 5.5635 |
| 0.0000 | - | - | - | - | - | 24.9266 | 5.5144 |

Fig. 1 shows the variation of velocity with mole fraction of MS (X_{MS}). It is clear from Fig. 1 that almost linear increase in velocity is observed in case of dioxane whereas nonlinear increase of velocity is observed in benzene and methanol system. Other properties also like Z , R , W , b etc., also increased with

X_{MS} in the same manner. However, K_s , L_f , π and r are observed to decrease with X_{MS} . These observations suggest increase in intermolecular forces, *i.e.*, strong interaction between MS and solvent¹³. Non-linear increase in U in MeOH suggest weak interaction in MeOH.

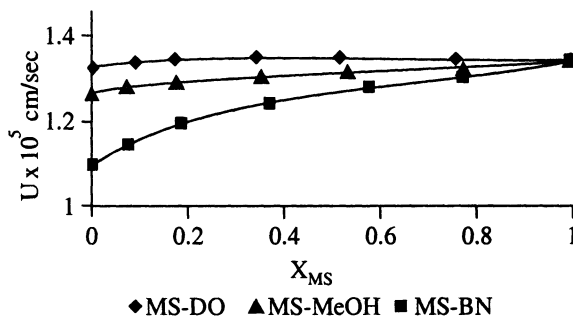


Fig. 1. Variation of velocity (U) with mole fraction of X_{MS}

A comparison of viscosity data of MS in the three solvents (Table-1) show almost linear increase of viscosity with mole fraction of MS in DO and MeOH whereas much variation in viscosity data in benzene shows more interaction in this system. This is again proved by internal pressure values (Table-2). Internal pressure is a measure of cohesive forces occurring in the system. It is observed that π decreases with X_{MS} indicating thereby decrease of cohesive forces with mole fraction. In MS-BN system, after 0.4 mole fraction of MS, increase in π values suggests much interaction which may be due to bonding between phenyl ring of benzene and MS. It is observed that interaction is less in MeOH (containing no ring structure), more in dioxane which has ring structure and maximum in benzene (having phenyl ring).

Further, both $(\alpha/f^2)_{Cl}$ and τ are dependent on U , ρ and η . $(\alpha/f^2)_{Cl}$ and τ and increased linearly and non-linearly respectively with mole fraction of MS. The contribution of acoustic relaxation is regarded due to entropic fluctuation associated in solution of dynamically formed physical entity.

It is evident from Table-4 that in MS-BN and MS-MeOH, excess volumes are negative up to 0.15 whereas in MS-DO system, values are positive except at 0.07 where it is negative. The negative values in MeOH and benzene system are due to breaking of bonds resulting in the reduction of apparent interacting distance as a whole whereas positive values at very low concentration of MS suggest that interactions are favoured by molecular packing at that concentration. Same is the reason for MS-DO system where presence of oxygen also causes an increase in excess volume.

Excess viscosity and excess velocity values are all negative for MS-DO and MS-BN systems whereas for MS-MeOH system, excess viscosity is negative only for one composition (0.07) and excess velocities are all positive.

Excess free energy of activation of flow are negative for MS-BN system only whereas positive for both MS-DO and MS-MeOH systems. Almost similar is the case for Grunberg-Nissan characteristic parameter (d) which gives approximate measure of strength of interaction between components of the mixture. Values of ΔG^E vary considerably in three systems. In MS-BN system, the values are all negative whereas for MS-DO and MS-MeOH systems, these are positive. Further, values are much higher for methanol system. The negative values of ΔG^E are due to dispersive forces or breaking of bonds of associated components. The positive values are due to specific interactions. Larger positive values may be due to difference in the sizes of the two components in the binary mixture.

Comparison of η^E , U^E , ΔG^E and d values show maximum positive values for methanol system confirming thereby more interaction of MS and MeOH, whereas for MS-BN system, all the three parameters have negative values, suggesting thereby that specific interactions are absent but dispersion forces are dominant in solution. Interaction is more in dioxane than in benzene system, due to the presence of lone pair of electrons of oxygen. Surface tension and molecular diameter values are found to increase with concentration of MS as expected.

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