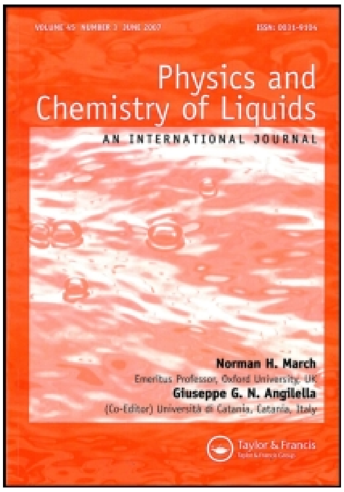

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Densities, Adiabatic Compressibility, Freelength, Viscosities and Excess Volumes of Dimethyl Sulfoxide with Some Aromatic Esters at 303.15-318.15 K

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DENSITIES, ADIABATIC COMPRESSIBILITY, FREELENGTH, VISCOSITIES AND EXCESS VOLUMES OF DIMETHYL SULFOXIDE WITH SOME AROMATIC ESTERS AT 303.15–318.15 K

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Measurements of density, ultrasonic velocity and viscosities for binary mixtures of methyl salicylate(1) + dimethyl sulfoxide(2), ethyl salicylate(1) + dimethyl sulfoxide(2), methyl benzoate(1) + dimethylsulfoxide(2) and benzyl salicylate(1) + dimethyl sulfoxide(2) respectively are reported from 303.15–318.15 K over the entire range of composition. Also other related physical parameters viz. adiabatic compressibility, excess adiabatic compressibility, intermolecular freelength, Rao's constant, Wada's constant, excess volume and excess viscosity have been computed. The extent and nature of interactions among the component liquids are discussed.

Keywords: Adiabatic compressibility; viscosity and excess volume

INTRODUCTION

We report here new experimental data for the binary liquid mixtures of dimethyl sulfoxide(2) with methyl salicylate(1), ethyl salicylate(1), methyl

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benzoate(1) and benzyl salicylate(1) respectively at 303.15–318.15 K. The group of liquids studied contains four binary systems in which dimethyl sulfoxide a polar, undissociated, aprotic solvent with high dielectric constant acts as a common component and three salicylate esters and methyl benzoate constitute non-common component. As dimethyl sulfoxide is widely used as a solvent for several industrial processes, the study of its interaction with esters will throw light on designing, separation operations such as distillation, extraction, crystallisation etc.. Moreover the survey of literature on ultrasonic studies reveals that extensive work on the liquid mixtures having weak interactions has been reported. Further the data of the title systems have been obtained at a range of temperatures with a view to understand the effect of temperature on these properties.

EXPERIMENTAL

Densities of liquids and liquid mixtures were determined by using bicapillary pycnometer [1] at 303.15–318.15K. The pycnometer was calibrated with deionized double distilled water. Density values are reproducible to $\pm 5\times 10^{-5}$ g.c.^{3} . Excess volumes were computed from density and comparities with the equation.

$$V^E = [XM_1 + (1-x)M_2]/\rho_m - XM_1/\rho_1 - (1-x)M_2/\rho_2 \qquad (1)$$

where X are the molefraction of salicylate/methyl benzoate, M_1, M_2 represent molecular masses and ρ_m, ρ_1, ρ_2 are the densities of the mixture component 1 and component 2 respectively.

Ultrasonic velocities were measured with a single crystal ultrasonic interferometer at a frequency of 2 MHz and these are accurate to ± 0.02. The measurements were made at 303.15, 308.15, 313.15 and 318.15 K. The temperature was maintained by circulating water around the liquid cell from a thermostat controlled to ± 0.01 K. Adiabatic compressibilities were calculated from the relation.

$$\beta_{\mathrm{ad}} = \frac{1}{U^2\rho} \qquad (2)$$

where U is the ultrasonic velocity. Deviations in excess adiabatic compressibility were obtained using the equation.

$$\beta_{\mathrm{ad}}{}^{E} = \beta_{\mathrm{ad}} - [\beta_{\mathrm{ad}_1} x + \beta_{\mathrm{ad}_2}(1-x)] \tag{3}$$

Where $\beta_{\mathrm{ad}}, \beta_{\mathrm{ad}_1}, \beta_{\mathrm{ad}_2}$ are the adiabatic compressibilities of the mixture and the pure components respectively.

Intermolecular free length (L_f) has been evaluated by Jacobson's formula [2, 3]

$$L_f = \mathrm{K}(\beta_{\mathrm{ad}})^{1/2} \tag{4}$$

Where K is Jacobson's constant which is temperature dependent [3]of the nature of the liquid. Rao's constant [4] has been calculated using the formula

$$\mathrm{R} = \frac{-\bar{\mathrm{M}}}{\rho} C^{1/3}$$

where $\bar{M} = x_1 M_1 + x_2 M_2$ which is the mean molecular weight

$$\therefore \mathrm{R} = \bar{V} C^{1/3} \tag{5}$$

Where $\bar{M}/\rho = \bar{V}$, ie the molar volume
Wada's constant [5] has been calculated using the formula

$$\mathrm{W} = \bar{V}(\beta_{\mathrm{ad}})^{-1/7} \tag{6}$$

Viscosities were measured using an Ostawald viscometer. The viscometer was calibrated at each temperature using distilled water. The viscometer constant K, was calculated from the viscosity, η_W, density, ρ_W, and flow time t_W of water using the relation $\mathrm{K} = \eta_W/\rho_W t_W$. The estimated error in viscosity was $\pm 5 \times 10^{-4}$ cp. The performance of the viscometer was assessed by measuring and comparing the viscosities of the pure component with the values reported in the literature. Experimental viscosity values were used to calculate η^E using the relation [6].

$$\eta^E = \eta_m \Sigma x_i \eta_i \tag{7}$$

Where η is the viscosity, superscript E stands for excess and subscripts i and m stand for pure components and the mixtures respectively.

The liquids methyl salicylate, ethyl salicylate, methyl benzoate and benzyl salicylate used were of AR(BDH) grade and were distilled and purified by standard methods described by Weissberger [7]. Dimethyl sulfoxide was purified by the method described by Gopal *et al.* [8]. Their purities were checked by measuring densities and comparing the data with these reported in literature [9, 10]. Solvent mixtures were prepared on weight/weight basis and the molefractions(x) were calculated from the weights and densities of individual components [11].

RESULTS AND DISCUSSION

The experimental densities (ρ) ultrasonic velocity (U), viscosities (η) and the derived adiabatic compressibility (β_{ad}), mean molecular weight ($\bar{M}$), mean molar volume ($\bar{V}$) and intermolecular free length (L_f) at 303.15 K over the whole range of composition for the four systems namely methyl salicylate(1), ethyl salicylate(1), methyl benzoate(1) and benzyl salicylate(1) with dimethyl sulfoxide(2), respectively are included in . The computed values of excess volume (V^E) excess adiabatic compressibility (β_{ad}^E), excess viscosity(η^E), Rao's constant(R), Wada's constant(W) at 303.15 K for the four binary systems are given in . The variation of velocity with the molefraction of alkyl/aryl ester at four different temperatures reveals that the velocity decreases almost steadily with increasing concentration of ester in a linear fashion for the temperature studied. The velocity at any concentration is decreasing as the temperature increases. The Variation of viscosity with the molefraction of alkyl/aryl ester at four different temperatures studied reveals that the viscosity increases non-linearly without going through any maxima. Very little variation is observed between the molefraction 0.4 and 1.0. The variation of adiabatic compressibility (βa_{ad}) and mean free length with the molefraction of alkyl/aryl ester at four different temperatures show an increasing trend at lower concentrations and more or less have the same values between 0.8 and 0.9 molefractions and slight decrease as molefraction approaches 1.0.

The variation of Rao's constant and Wada's constant with molefraction of alkyl/aryl ester indicated that it is increasing with molefraction.

TABLE I Molefraction (x), density(ρ), ultrasonic velocity(u), viscosity(η) adiabatic compressibility(β_{ad}) Mean molecular weight($\bar{M}$), Mean molar volume($\bar{V}$) and Intermolecular free length (L_f) at 303.15 K

X	$\rho(g.cm^{-3})$	U ms^{-1}	η cp	$\beta_{ad} \times 10^{12}$ $(cm^2/dyne)$	$\bar{M}$ (g)	$\bar{V}(g)$ (cm^3/mol^{-1})	Lf A^0
Methyl salicylate (1) + dimethylSulfoxide (2) at 303.15 K							
0.0000	1.0890	1469.6	1.730	42.51	78.13	71.74	0.4088
0.1215	1.1060	1450.4	1.932	42.98	87.12	78.77	0.4111
0.1918	1.1160	1446.4	2.130	42.83	92.33	82.73	0.4103
0.2697	1.1240	1435.2	2.186	43.19	98.09	87.27	0.4121
0.3567	1.1320	1425.6	2.283	43.46	104.53	92.34	0.4134
0.5628	1.1450	1413.6	2.356	43.59	119.79	104.34	0.4139
0.6882	1.1570	1403.2	2.380	43.89	129.07	111.56	0.4154
0.8323	1.1630	1394.4	2.403	44.22	139.74	120.15	0.4169
1.0000	1.1750	1390.4	2.440	44.02	152.15	129.49	0.4160
Ethyl salicylate(1) + dimethyl sulfoxide(2) at 303.15 K							
0.0000	1.0890	1469.6	1.730	42.52	78.13	71.74	0.4088
0.0499	1.0930	1461.6	1.888	42.83	82.52	75.50	0.4103
0.1687	1.0980	1437.6	2.196	44.07	92.98	84.68	0.4162
0.2404	1.1000	1428.0	2.294	44.58	99.29	90.27	0.4186
0.3226	1.1030	1414.2	2.533	45.32	106.53	96.58	0.4221
0.4179	1.1070	1403.2	2.570	45.38	114.92	103.81	0.4247
0.5265	1.1090	1394.4	2.723	46.38	124.48	112.25	0.4270
0.6564	1.1110	1382.4	2.843	47.10	135.92	122.34	0.4303
1.0000	1.1180	1354.4	3.117	48.76	166.17	148.63	0.4378
Methyl benzoate(1) + dimethyl sulfoxide(2) at 303.15 K							
0.0000	1.8090	1469.0	1.730	42.52	78.13	71.74	0.4088
0.1946	1.0850	1451.2	1.1775	43.76	89.40	82.40	0.4148
0.2734	1.0820	1437.0	1.752	44.72	93.99	86.87	0.4193
0.3608	1.0800	1432.0	1.751	45.15	99.06	91.72	0.4213
0.4584	1.0790	1424.0	1.751	45.70	104.73	97.06	0.4239
0.5683	1.0760	1412.0	1.723	46.61	111.10	103.26	0.4281
0.6931	1.0730	1408.0	1.682	47.01	118.34	110.29	0.4299
1.0000	1.0710	1380.0	1.583	49.03	136.15	127.12	0.4390
Benzyl salicylate(1) + dimethyl sulfoxide(2) at 303.15 K.							
0.0000	1.0890	1469.6	1.730	42.52	78.63	71.74	0.4088
0.0790	1.1925	1481.6	2.299	41.70	89.99	82.37	0.4049
0.1284	1.1942	1481.6	2.529	41.63	97.40	89.02	0.4046
0.1867	1.0956	1481.6	2.933	41.51	106.15	96.89	0.4043
0.2564	1.0975	1481.6	3.273	41.51	116.62	106.26	0.4039
0.3413	1.0988	1488.8	3.776	41.06	129.36	117.73	0.4017
0.4467	1.1013	1488.8	4.342	40.97	145.18	131.83	0.4013
0.5812	1.1031	1490.4	4.995	40.81	165.37	149.92	0.4005
1.0000	1.1065	1498.4	6.722	40.25	228.24	206.27	0.3978

Note: Tables are available for other temperatures

TABLE II Molefraction, excess volume, excess compressibility, express viscosity, Rao's constant and Wada's constant at 303.15 K

X	V^E *cm²/mol*	$\beta_{ad}^E \times 10^{12}$ *cm²/dyne*	η^E *cp*	*Rao's Constant*	*Wada's Constant*
Methyl Salicylate(1) + dimethyl sulfoxide(2) at 303.15 K					
0.0000	0.000	0.0000	0.000	815.7	2174.8
0.1215	0.013	0.2793	0.116	891.7	2384.2
0.1918	−0.090	0.0243	0.264	935.6	2505.2
0.2697	−0.047	0.2685	0.265	984.4	2639.5
0.3567	0.001	0.4118	0.300	1039.3	2790.4
0.5628	0.102	0.2266	0.226	1171.1	3151.8
0.6882	0.072	0.3423	0.161	1248.9	3366.3
0.8323	0.346	0.4518	0.802	1342.3	3621.8
1.0000	0.000	0.0000	0.000	1445.3	3905.8
Ethyl salicylate(1) + dimethyl sulfoxide(2) at 303.15 K					
0.0000	0.000	0.0000	0.000	815.7	2174.8
0.0499	−0.079	−0.0021	0.089	856.8	2286.3
0.1687	−0.032	0.4967	0.232	955.7	2553.9
0.2404	0.039	0.5624	0.231	1016.5	2747.8
0.3226	0.035	0.7872	0.356	1080.2	2901.2
0.4179	−0.062	0.7523	0.260	1162.2	3112.9
0.5265	0.022	0.5715	0.263	1254.0	3360.6
0.6564	0.127	0.4841	0.203	1362.8	3654.7
1.0000	0.000	0.0000	0.000	1644.5	4418.2
Methyl benzoate(1) + dimethyl sulfoxide(2) at 303.15 K					
0.0000	0.000	0.0000	0.000	815.7	2174.8
0.1946	−0.106	−0.0127	0.074	932.9	2487.6
0.2734	−0.016	0.4213	0.062	980.4	2614.4
0.3608	−0.000	0.2862	0.074	1033.9	2756.7
0.4584	−0.072	0.2018	0.088	1091.9	2911.9
0.5683	0.039	0.3960	0.076	1158.4	3089.1
0.6931	0.164	−0.0202	0.054	1236.2	3295.7
1.0000	0.000	0.0000	0.000	1415.3	3775.9
Benzyl salicylate(1) + dimethyl sulfoxide(2) at 303.15 K					
0.0000	0.000	0.0000	0.000	815.7	2174.8
0.0790	−0.003	−0.6410	0.175	939.0	2503.8
0.1284	0.001	−0.5939	0.158	1014.8	2706.6
0.1867	0.032	−0.5150	0.271	1104.6	2946.5
0.2564	0.021	−0.4290	0.263	1211.4	3232.1
0.3413	0.072	−0.6858	0.342	1344.3	3586.6
0.4467	−0.008	−0.5402	0.382	1505.3	4017.5
0.5812	−0.014	−0.3901	0.363	1712.5	4571.2
1.0000	0.000	0.0000	0.000	2360.4	6301.9

Note: Tables are available for other temperatures

Further, over the temperature range 303.15–318.15 K, the variation in these constants is almost negligible for any particular composition. The variation of excess viscosity with the molefraction of the ester at different temperature studied shows that the excess viscosity is positive and reaches a broad maximum around 0.3 and 0.4 molefractions for all the temperatures in all the systems. The variation of excess adiabatic compressibility with molefraction of methyl salicylate, ethyl salicylate, methyl benzoate and benzyl salicylate systems respectively in indicates positive excess adiabatic compressibility reaching maximum at about 0.5 molefractions for all the temperature studied.

The ultrasonic velocity, freelength and compressibility for the first three systems studied show a little deviation from the linear variation with the molefractions of the aromatic ester indicating the dominance of dispersive forces over the other strong interactions. The variations of velocity and compressibility with molefraction of ester do not exhibit any minimum in velocity nor any dip in compressibility, there by indicating the absence of complex formation. In the case the benzyl salicylate and dimethyl sulfoxide, the velocity results show non-linear variations indicating strong intereactions between the molecules. Salicylates are known to exist the selfassociated molecules forming intermolecular hydrogen bonding through the carbonyl oxygen and OH group in ortho position. Polar impurity atoms like dimethyl sulfoxide can produce dispersive influence on the self associated structure by breaking the hydrogen bonds. This process produces decrease in viscosity and positive excess compressibilities large excess volumes, positive excess compressibility, positive mean free length in the case of methyl salicylate, and ethyl salicylate with dimethyl sulfoxide are in accordance with this agreement. The results are in good agreement with earlier reports [12, 13]. The positive excess compressibilities in the case of methyl benzoate and dimethyl sulfoxide also indicate that dispersive forces are operative between the molecules [13]. However the important departure from this trend is to be noted with velocity values of benzoyl salicylate and dimethyl sulfoxide system. The velocity varies non linearly with the concentration of the ester indicating strong interaction between the molecules. This could be observed from the large negative excess compressibility values and it appears that the strength of inter molecular interaction between the molecules increase when the aliphatic alkyl groups in salicylate ester is replaced by aryl group. This observation can be explained by considering the fact that the aryl group has a tendency to withdraw electrons, thus lowers the electron density on carbonyl oxygen. This process reduces the strength of inter molecular hydrogen bonding between the carbonyl oxygen and OH group at the salicylates. As a result, the polar molecules like dimethyl sulfoxide find it access to have strong molecular interaction by way of forming hydrogen bonding with OH group of ester replacing the intermolecular hydrogen bonding. The experimental observations in the case of benzyl salicylate and dimethyl sulfoxide indicates that the β^E values are negative with a minimum at an intermediate concentrations and is altogether different from the observed trend in the first two systems, which seem to present only positive excess compressibility. This is in support of the argument that the intermolecular interaction is strongest in the case of benzyl salicylate and dimethyl sulfoxide and decrease systematically when the aryl group is replaced by methyl and ethyl groups. Because methyl and ethyl groups are capable of releasing electrons causing greater strength to the inter molecular hydrogen bonding in the salicylate, the dimethyl sulfoxide molecules find it difficult to form hydrogen bonding with the salicylates. With regard to methyl benzoate and dimethyl sulfoxide, the ester is a weakly polar liquid while dimethyl sulfoxide is polar. When dimethyl sulfoxide is added to methyl benzoate the weak dipole induced dipole interactions should occer between the molecules. However dispension forces are giving riseto positive deviations in excess volume, excess compressibility as in the case of the first two systems. This shows the absence of specific interactions between the molecules. This is in agreement with the earlier reports [14]. Basing on the positive values of the excess compressibility which is a measure of the strength of interaction, the order of interaction of aromatic esters with dimethyl sulfoxideis as follows: benzyl salicylate > ethyl salicylate > methyl salicylate > methyl benzoate. Another interesting parameter representative of structural adjustment in solution is intermolecular freelength. Variation of L_f is a function of composition and temperature in the first three systems indicates that L_f increases with the composition probably due to the breaking of intermolecular hydrogen bonds by the polar molecules in the case of first two systems while dispersion forces between unlike molecules result in the increase of freelength in the case of third system. Though strong interactions between unlike molecules are involved in benzyl salicylate and dimethyl sulfoxide, the very small increase in L_f is also attributed due to the breaking of inter hydrogen bonding in the ester followed by the specific interactions between the molecules. The existance of structurally different species in solution is bound to have its effect reflected in the physical parameters like excess volume also. The positive excess volume in the first three systems indicate that the effects leading to expansion in volume is dominant over the effect leading to contraction in volume. The small positive and negative values of V^E for the binary system of benzyl salicylate and dimethyl sulfoxide may be attributed to a resultant contributions of the factors leading to expansion and contraction.

The apparent excess viscosity(η^E) of the mixtures has been computed from the viscosities of the mixtures and of the pure component viscosities. The computed values are small positive for all the mixtures at all temperatures. The excess values should be atleast slightly negative to corraborate the results of the excess compressibilities. This may be ascribed due to the influence of molar structure of aromatic esters of viscosity [15]. Further more, the sign and magnitude of η^E depends on the combinded effect of the factors like molecular size and shape of the components in addition to intermolecular forces. The values of η^E are decreasing systematically with increasing temperature of all the mixtures.

The observed small positive excess viscosities in all the systems of DMSO with aromatic esters indicate that the factors leading to both the aspects are affecting the systems.

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