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Excess thermodynamic studies in binary liquid mixtures of 2-methyl-2-propanol with ketones at 298.15, 303.15 and 308.15 K

K. Rajagopal [a], S. Chenthilnath [b,*]

[a] Department of Physics, Govt. College of Engineering, Tirunelveli – 627 007, Tamilnadu, India
[b] Department of Physics, Satyam College of Engineering and Technology, Nagercoil – 629 301, Tamilnadu, India

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ABSTRACT

Densities, ρ, ultrasonic speeds, u, and viscosities, η of binary mixtures of 2-methyl-2-propanol (2M2P) with acetone (AC), ethyl methyl ketone (EMK) and acetophenone (AP) including those of pure liquids are measured over the entire composition range at temperatures 298.15, 303.15 and 308.15 K respectively. From these experimental data, the excess available volume, V_a^E, excess free volume, V_f^E, excess free energy of activation, ΔG^{*E}, deviations in isentropic compressibility, Δk_s and ultrasonic speed, Δu and excess molar isentropic compressibility, $K_{s,m}^E$ are calculated and reported. The variation of these properties with composition and temperature are discussed in terms of molecular interactions between unlike molecules of the mixtures. Furthermore, the theoretical viscosities have been evaluated using four standard models and the relative merits are discussed.

1. Introduction

Ultrasonic waves have acquired the status of an important probe for the study of structure and properties of matter. The use of ultrasound is one of the well recognized approaches for the study of molecular interactions in fluids. Ultrasonic speed plays an important role in the investigation of intermolecular interactions. The structural arrangements are influenced by the shape of the molecules as well as by their mutual interactions [1]. The present work is the continuation of our earlier studies [2,3] on thermodynamic properties of binary mixtures, which have relevant industrial applications. In this report, we present the density, ρ ultrasonic speed, u, and viscosity, η values of pure 2-methyl-2-propanol (2M2P), acetone (AC), ethyl methyl ketone (EMK) and acetophenone (AP) and those of their binary mixtures over the entire composition range at 298.15, 303.15 and 308.15 K respectively. From the measured values, some of the excess parameters like V_a^E, V_f^E, ΔG^{*E}, Δk_s, Δu and $K_{s,m}^E$ are calculated and reported in terms of molecular interactions between unlike molecules of the mixtures. In addition to this, the theoretical viscosities of the binary mixtures have been evaluated using four standard models and the relative merits are discussed.

2. Experimental

2M2P (Ranchem, India, purity >99.7%), AC, EMK and AP (s.d. fine Chemicals, India, purity > 99%) were purified by using the methods described in the literature [4,5] and only middle fractions were used in the experiment. All the chemicals were stored over 0.4 nm molecular sieves to remove water content and degassed just before use. The mixtures were prepared by mass and were kept in special airtight stopper glass bottles to avoid evaporation. The weighings were done by using an electronic balance (AND, HR series 300, Japan) with a precision of ± 0.1 mg. The uncertainty in the mole fraction was estimated to be less than $\pm 1 \cdot 10^{-4}$.

Densities, ultrasonic velocities and viscosities of the pure liquids and their binary mixtures were measured by using a single capillary pycnometer, single-crystal variable-path multifrequency ultrasonic interferometer (Model no. F-05, Mittal enterprises, New Delhi) at 2 MHz, Ubbelohde type suspended level viscometer and the details are reported elsewhere [2,6–8]. The reproducibility in the above measured parameters are ± 0.1 kg m^{-3}, $\pm 0.03\%$ and $\pm 2 \cdot 10^{-6}$ N s m^{-2} respectively. The temperature of the test liquids (Eurotherm, Mittal Enterprises, India) during the measurements was maintained within an uncertainty of ± 0.01 K in an electronically controlled thermostatic water bath.

The reliability of experimental measurements of ρ, u and η were ascertained by comparing the experimental data of pure liquids with the corresponding literature values (see Table 1).

3. Results and discussions

The experimental values of densities, ρ, ultrasonic speeds, u and viscosities, η of binary mixtures of 2M2P with AC, EMK and AP, over the entire composition range, expressed in terms of mole fraction, x_1 of 2M2P at various temperatures are listed in Table 2. As thermodynamic excess functions are generally sensitive to intermolecular

* Corresponding author. Tel.: +91 9443418697; fax: +91 4652 227621.
E-mail address: chenthilnaths@rediffmail.com (S. Chenthilnath).

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Table 1
Comparison of experimental values of density, ρ, viscosity, η and ultrasonic speed, u, of pure liquids with the corresponding literature values at different temperatures.

Liquids	ρ (kg m^{-3})		η (10^{-3} N s m^{-2})		u (m s^{-1})	
	Exp	Lit	Exp	Lit	Exp	Lit
298.15 K						
2-methyl-2-propanol	780.8	780.9 [9]	4.3898	4.3915 [10]	1121.2	1123.5 [10]
AC	784.3	784.89 [11]	0.3027	0.306 [12]	1162.0	1163 [13]
EMK	798.2	798.1 [14]	0.3856	0.3855 [15]	1191.6	1191.2 [16]
AP	1022.4	1022.5 [17]	1.6788	1.681 [12]	1476.2	–
303.15 K						
2-methyl-2-propanol	775.3	775 [18]	3.3792	3.379 [10]	1102.3	1104.8 [19]
AC	779.7	779.1 [20]	0.2918	0.293 [20]	1141.2	1140 [20]
EMK	794.7	794.5 [21]	0.3653	0.323 [22]	1173.5	1173 [21]
AP	1017.9	–	1.5328	–	1457.2	1457 [23]
308.15 K						
2-methyl-2-propanol	770.1	–	2.6427	2.6448 [10]	1082.8	–
AC	773.5	773.9 [20]	0.2809	0.280 [20]	1121.4	1122 [20]
EMK	788.5	788.8 [15]	0.3440	0.3441 [15]	1153.8	1153.3 [15]
AP	1013.5	–	1.4073	–	1441.2	1440 [14]

interactions, many authors in literature have used the excess parameters to identify the strength of interactions between unlike molecules of mixtures [24,25].

The excess functions such as V_a^E, V_f^E and ΔG^{*E} are calculated using the relation,

$$Y^E = Y - [x_1 Y_1 + x_2 Y_2] \quad (1)$$

where Y^E represents V_a^E, V_f^E and ΔG^{*E} of the mixture; x is the mole fraction, subscripts 1 and 2 refer to 2M2P and AC/EMK/AP respectively.

The deviations in isentropic compressibility, Δk_s and ultrasonic speed, Δu and excess molar isentropic compressibility $K_{s,m}^E$ are calculated using the following standard relations [26,27] and are listed in Table 2.

$$\Delta k_s = k_s - k_s^{id} \quad (2)$$

$$\Delta u = u - \left(\rho^{id} k_s^{id}\right)^{-1/2} \quad (3)$$

$$K_{s,m}^E = K_{s,m} - K_{s,m}^{id} \quad (4)$$

In the above equations, the superscript "id" represents the ideal mixture; and the values of k_s, $\rho^{id}$and k_s^{id} are calculated using the following relations [27]

$$k_s = \frac{1}{u^2 \rho} \quad (5)$$

Table 2
Densities, ρ, ultrasonic velocities, u, viscosities, η, available volume, V_a, free volume, V_f and free energy of activation, ΔG^*, deviations in isentropic compressibility, Δk_s and ultrasonic speed, Δu and excess molar isentropic compressibility, $K_{s,m}^E$ as functions of mole fraction, x_1 of 2M2P for 2M2P + AC/EMK/AP binary mixtures at 298.15 K.

x_1	ρ	u	$\eta \times 10^3$	$V_a \times 10^6$	$V_f \times 10^{18}$	ΔG^*	$\Delta k_s \times 10^{10}$	$\Delta u \times 10^{-2}$	$K_{s,m}^E \times 10^{14}$
	kg m^{-3}	m s^{-1}	N s m^{-2}	m^3 mol^{-1}	m^3 mol^{-1}	J mol^{-1}	m^2 N^{-1}	m s^{-1}	m^2 N^{-1}
2M2P + AC									
0.0000	784.3	1162.0	0.3027	20.2721	1.0854	27,109	0.0000	0.0000	0.0000
0.0784	783.8	1153.2	0.3321	21.1406	1.0768	27,393	0.0766	−0.0452	0.0594
0.1618	783.3	1146.4	0.3734	21.9602	1.0582	27,740	0.1217	−0.0702	0.0972
0.2497	782.8	1140.3	0.4146	22.7872	1.0359	28,058	0.1567	−0.0887	0.1287
0.3433	782.3	1134.8	0.4676	23.6326	1.0100	28,417	0.1821	−0.1012	0.1541
0.4398	781.9	1130.1	0.5414	24.4650	0.9812	28,842	0.1952	−0.1071	0.1693
0.5382	781.7	1126.9	0.6566	25.2349	0.9476	29,380	0.1822	−0.0997	0.1610
0.6472	781.5	1124.6	0.8929	26.0288	0.9083	30,207	0.1499	−0.0818	0.1352
0.7532	781.3	1122.9	1.3036	26.7775	0.8710	31,206	0.1130	−0.0615	0.1039
0.8729	781.1	1121.6	2.1307	27.5923	0.8297	32,491	0.0641	−0.0351	0.0598
1.0000	780.8	1121.2	4.3898	28.4073	0.7863	34,353	0.0000	0.0000	0.0000
2M2P + EMK									
0.0000	798.2	1191.6	0.3856	23.0595	0.6178	28,201	0.0000	0.0000	0.0000
0.0925	796.3	1177.8	0.3917	23.9572	0.6493	28,253	0.0969	−0.0619	0.0902
0.1893	794.3	1166.9	0.4117	24.7039	0.6751	28,389	0.1528	−0.0941	0.1443
0.2885	792.3	1157.3	0.4407	25.3848	0.6986	28,571	0.1914	−0.1142	0.1831
0.3835	790.5	1148.8	0.4875	25.9992	0.7200	28,833	0.2213	−0.1289	0.2130
0.4877	788.6	1140.6	0.5818	26.6118	0.7411	29,284	0.2399	−0.1365	0.2324
0.5862	787.0	1134.8	0.7295	27.0757	0.7557	29,857	0.2261	−0.1265	0.2195
0.6907	785.4	1129.7	0.9865	27.5069	0.7684	30,617	0.1952	−0.1078	0.1897
0.7895	783.9	1125.8	1.4236	27.8631	0.7777	31,538	0.1523	−0.0831	0.1482
0.8935	782.4	1122.4	2.2527	28.1965	0.7854	32,687	0.0960	−0.0522	0.0928
1.0000	780.8	1121.2	4.3898	28.4073	0.7863	34,353	0.0000	0.0000	0.0000
2M2P + AP									
0.0000	1022.4	1476.2	1.6788	9.0929	0.0663	32,500	0.0000	0.0000	0.0000
0.1188	999.9	1441.3	2.0807	11.3761	0.0828	32,971	−0.2887	0.4050	−0.3383
0.2314	977.7	1407.2	2.4562	13.4955	0.1035	33,324	−0.5139	0.6341	−0.5922
0.3395	955.0	1373.3	2.8002	15.5074	0.1298	33,592	−0.6897	0.7573	−0.7799
0.4286	935.6	1344.9	3.0796	17.1130	0.1577	33,779	−0.8093	0.8066	−0.9024
0.5450	908.5	1305.2	3.4201	19.2796	0.2073	33,976	−0.9015	0.7919	−0.9851
0.6429	883.8	1268.4	3.6515	21.2356	0.2671	34,086	−0.8936	0.7054	−0.9577
0.7373	858.6	1231.8	3.8559	23.1069	0.3461	34,171	−0.8153	0.5799	−0.8570
0.8283	832.9	1194.8	4.0336	24.9399	0.4521	34,235	−0.6466	0.4153	−0.6664
0.9142	807.7	1159.4	4.2080	26.6168	0.5892	34,293	−0.4015	0.2324	−0.4083
1.0000	780.8	1121.2	4.3898	28.4073	0.7863	34,353	0.0000	0.0000	0.0000

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