

Research Article

Thermophysical Properties of Binary Liquid Systems of Ethanoic Acid, Propanoic Acid, and Butanoic Acid with Benzene or Acetophenone

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The density (ρ), viscosity (η), and surface tension (σ) of binary mixtures of carboxylic acids (CAs) (ethanoic acid (EA), propanoic acid (PA), butanoic acid (BA)) + benzene (BEN) or acetophenone (ACT) have been measured at 298.15, 308.15, and 318.15 K. From the experimental results, excess values of molar volume (V^E), viscosity (η^E), Gibbs's free energy for the activation of low (G^E), and surface tension (σ^E) were evaluated and fitted to a Redlich-Kister type of equation. The parameter “ d ” of Grunberg and Nissan expression has also been calculated. From the sign and magnitude of V^E , η^E , G^E , σ^E , and “ d ” values, it is concluded that specific interactions are present in CA+ACT system and these interactions are absent in CA + BEN mixtures. Various viscosity and surface tension models have been used to test the consistency of the data.

1. Introduction

Studies on thermophysical properties of binary liquid mixtures containing carboxylic acids are not extensive [1–3]. In view of this, we have undertaken studies on binary mixtures of carboxylic acids (CAs), namely, ethanoic acid (EA), propanoic acid (PA), and butanoic acid (BA) which are self-associated solvents, with a nonpolar solvent benzene (BEN) and polar acetophenone (ACT). These acids exist as cyclic dimers in the pure state. However, trimers also exist which are formed because of strong interactions between ring dimers and monomers [4–6].

The excess properties V^E , η^E , G^E , σ^E , and Grunberg and Nissan parameter “ d ” computed from the experimental data (density (ρ), viscosity (η), and surface tension (σ)) of binary mixtures of carboxylic acids (EA, PA, BA) with benzene and acetophenone have been determined. Benzene interacts with acid through Vander Waal's or London dispersion forces and acetophenone forms chemical aggregates with acid through hydrogen bonding. The results are used to theoretically justify the validity of various viscosity and surface tension models. The main thrust of the investigation is to correlate the

experimental data in terms of the interacting components of the mixtures and to stress the factors affecting these interactions.

2. Experimental Section

Ethanoic acid, propanoic acid, butanoic acid, benzene, and acetophenone were purified by the standard methods described in the literature [7]. Ethanoic acid (BDH, 99% assay) was washed with a calculated amount of acetic anhydride for about 10 h and was subjected to fractional distillation. Propanoic acid and butanoic acid (E. Merck, 99% assay) were dried over anhydrous sodium sulfate for two days and the samples were distilled over potassium permanganate. Benzene (E. Merck, 98.4% assay) was dried by keeping over anhydrous calcium chloride for six to eight hours and then fractionally distilled. Acetophenone (Merck, 99% assay) was also dried by keeping it over anhydrous calcium chloride for two days and distilled at reduced pressure. The purity of all the components was checked by comparing their experimental densities with that of the literature values [7]. For each run, a fresh liquid mixture was prepared on a mass basis (precision

TABLE 1: Densities ($10^{-3}\rho$, kg m^{-3}) of the pure components at 298.15 K.

Component	This work	Lit. values [5]
Ethanoic acid	1.0437	1.04366
Propanoic acid	0.9882	0.9880
Butanoic acid	0.9533	0.9532
Benzene	0.8782	0.8737
Acetophenone	1.0241	1.0238

of 1×10^{-5} g). The purity of each component with respect to the corresponding literature value is recorded in Table 1.

Densities (ρ) of the pure components and their mixtures were measured with a density meter (AP, DMA-48) calibrated at each temperature with ethanol and 1,2-dichloroethane. The densities were measured with an accuracy of $1 \times 10^{-1} \text{ kg m}^{-3}$.

Viscosities (η) were determined using a modified Ubbelohde viscometer [8]. At each temperature, the viscometer was calibrated against the known viscosities of benzene and carbon tetrachloride [9]. The viscometer constants at each temperature were determined from the following

$$\frac{\eta}{\rho} = at - \frac{b}{t}, \quad (1)$$

where a and b are the temperature-dependent constants. At a particular temperature, an average value of the five consistently measured efflux times t and the densities were used to calculate viscosity. The accuracy of the viscosity measurements is in the order of $\pm 0.0013 \text{ mPa s}$.

Surface tension (σ) of the pure components and their mixtures was determined by the differential capillary rise method [7], using (2). The difference Δh in the liquid levels in two capillaries was measured with a cathetometer reading to 0.05 mm with a vernier constant of 0.01 mm. The surface tension values are accurate to within $\pm 0.02 \text{ mN m}^{-1}$. Consider

$$\Delta h = h_1 - h_2 = \frac{2\sigma}{\rho g} A + (B - C), \quad (2)$$

where $A = 1/r_1 - 1/r_2$, $B = (1/3)(r_2 - r_1)$, $C = 0.129(r_2^2/h_2)$, h_1 and h_2 are the heights of liquids in capillaries 1 and 2, r_1 and r_2 are the radii of the capillaries, and g is the acceleration due to gravity ($=9.80 \text{ m s}^{-2}$), respectively. The constants A , B , and C of (2) were determined by measuring the Δh for two test liquids (benzene, ethyl ethanoate) of known σ and ρ at 298.15 K. The constant C was separately determined by noting the height of the test liquid in one of the capillaries. The corresponding radius r_2 of the capillary was determined from the measured weight of the mercury column of known length. The constants (A , B , and C) were assumed to be temperature independent. For each mixture of the respective systems and pure components, Δh was recorded at three different temperatures over the entire composition range.

All the measurements were made at a constant temperature that was maintained with the help of a circulating type ultra cryostat (type MK 70, MLW, Germany) within $\pm 0.02^\circ\text{C}$.

3. Results

Experimental densities of pure components and their literature values at 298.15 K are given in Table 1. Experimental values of ρ , η , and σ were fitted to (3) using nonlinear regression technique [10]. The computed coefficients of (3) and standard errors are listed in Table 3.

Equation (3) fits the experimental data within the average uncertainty in the temperature range of 298.15 K–318.15 K and $0 < x_1 < 1$

$$Y(T, x_1) = [a_0 \exp(a_1 T) (b_0 + b_1 x_1 + b_2 x_1^2 + b_3 x_1^3)]^{1/2}. \quad (3)$$

Based on the regular solution theory [11], Grunberg and Nissan proposed an empirical expression for viscosities of real mixtures:

$$d = \frac{1}{(x_1 x_2)} [\ln \eta_{\text{mix}} - x_1 \ln \eta_1 - x_2 \ln \eta_2], \quad (4)$$

where η_1 and η_2 refer to the dynamic viscosities of the pure liquid components 1 and 2, respectively, x_1 and x_2 are the mole fractions of components 1 and 2, respectively, in the mixture, and “ d ” is a parameter which denotes the measure of strength of interaction between the two components. The values of “ d ” are reported in Table 2.

From the experimental data, excess molar properties, namely; V^E , η^E , G^E , and σ^E were calculated [12] from the following expressions:

$$V^E (\text{cm}^3 \text{ mol}^{-1}) = x_1 M_1 \left[\frac{1}{\rho_{\text{mix}}} - \frac{1}{\rho_1} \right] + x_2 M_2 \left[\frac{1}{\rho_{\text{mix}}} - \frac{1}{\rho_2} \right],$$

$$\log_{10} \left(\frac{1}{\eta^0} \right) = x_1 \log_{10} \left(\frac{1}{\eta_1} \right) + x_2 \log_{10} \left(\frac{1}{\eta_2} \right), \quad (5)$$

$$\eta^E (\text{mPa s}) = \eta_{\text{mix}} - \eta^0, \quad (6)$$

$$\frac{G^E}{RT} (\text{J mol}^{-1}) = [\ln \eta_{\text{mix}} V_{\text{mix}} - (x_1 \ln \eta_1 V_1 + x_2 \ln \eta_2 V_2)], \quad (7)$$

$$\sigma^E (\text{mN m}^{-1}) = \sigma_{\text{mix}} - [x_1 \sigma_1 + x_2 \sigma_2], \quad (8)$$

where M_1 and ρ_1 are the molecular weight and density of the carboxylic acids. The same symbols with subscript 2 refer to BEN or ACT, respectively. V_1 , V_2 , and V_{mix} are the molar volumes and σ_1 , σ_2 , and σ_{mix} are the surface tension of the 1st, and 2nd components and mixture, respectively.

Graphical representations of V^E , η^E , G^E , and σ^E as a function of the mole fraction (x_1) of CA are given in Figures 1–8, respectively. Each of these functions, $F = V^E$, η^E , G^E and σ^E , has been fitted to the Redlich-Kister relation [13]:

$$F = x_1 x_2 \sum_{j=1}^n A_{j-1} (2x_1 - 1)^{j-1}, \quad (9)$$

where A_0 , A_1 , and A_2 are adjustable parameters and have been evaluated by the method of least squares. The value of

TABLE 2: Mole fraction of first component x_1 , density, viscosity, and surface tension for various systems.

(a) System: ethanoic acid (1) + benzene (2)												
Temp.	$T = 298.15, \text{ K}$				$T = 308.15, \text{ K}$				$T = 318.15, \text{ K}$			
x_1	$10^{-3} \rho,$ kg m^{-3}	$\eta, \text{ mPa s}$	$10^3 \sigma,$ N m^{-1}	d	$10^{-3} \rho,$ kg m^{-3}	$\eta, \text{ mPa s}$	$10^3 \sigma,$ N m^{-1}	d	$10^{-3} \rho,$ kg m^{-3}	$\eta, \text{ mPa s}$	$10^3 \sigma,$ N m^{-1}	d
0.0000	0.8782	0.6035	28.21	—	0.8669	0.5294	26.75	—	0.8560	0.4588	25.24	—
0.1465	0.8899	0.6157	28.02	−0.5760	0.8792	0.5599	26.63	−0.2350	0.8685	0.4941	25.20	−0.0080
0.2786	0.9035	0.6165	27.89	−0.7652	0.8926	0.5451	26.54	−0.6631	0.8822	0.4746	25.18	−0.5441
0.3984	0.9181	0.6258	27.73	−0.8931	0.9073	0.5380	26.46	−0.9022	0.8967	0.4682	25.16	−0.7692
0.5074	0.9335	0.6517	27.61	−0.9683	0.9226	0.5528	26.39	−1.0121	0.9119	0.4941	25.15	−0.7465
0.6071	0.9496	0.6964	27.51	−0.9991	0.9387	0.5906	26.33	−1.0263	0.9279	0.5477	25.14	−0.5641
0.6986	0.9666	0.7587	27.41	−0.9972	0.9556	0.6470	26.28	−0.9831	0.9449	0.6167	25.13	−0.2991
0.7829	0.9845	0.8364	27.33	−0.9733	0.9737	0.7158	26.23	−0.9122	0.9629	0.6859	25.13	0.0009
0.8607	1.0032	0.9265	27.25	−0.9330	0.9924	0.7904	26.18	−0.8450	0.9817	0.7418	25.12	0.3209
0.9329	1.0229	1.0263	27.17	−0.8784	1.0120	0.8647	26.14	−0.8561	1.0012	0.7728	25.12	0.6777
1.0000	1.0437	1.1310	27.10	—	1.0325	0.9487	26.10	—	1.0213	0.7667	25.11	—
(b) System: propanoic acid (1) + benzene (2)												
Temp.	$T = 298.15, \text{ K}$				$T = 308.15, \text{ K}$				$T = 318.15, \text{ K}$			
x_1	$10^{-3} \rho,$ kg m^{-3}	$\eta, \text{ mPa s}$	$10^3 \sigma,$ N m^{-1}	d	$10^{-3} \rho,$ kg m^{-3}	$\eta, \text{ mPa s}$	$10^3 \sigma,$ N m^{-1}	d	$10^{-3} \rho,$ kg m^{-3}	$\eta, \text{ mPa s}$	$10^3 \sigma,$ N m^{-1}	d
0.0000	0.8782	0.6035	28.21	—	0.8669	0.5294	26.75	—	0.8560	0.4588	25.24	—
0.1164	0.8877	0.6299	27.79	−0.1880	0.8766	0.5533	26.38	−0.1531	0.8658	0.4809	24.95	−0.0851
0.2287	0.8974	0.6452	27.42	−0.3151	0.8863	0.5619	26.06	−0.3290	0.8756	0.4889	24.69	−0.2620
0.3254	0.9063	0.6617	27.12	−0.3742	0.8954	0.5722	25.80	−0.4092	0.8847	0.5081	24.47	−0.2471
0.4415	0.9178	0.6954	26.76	−0.3831	0.9071	0.5995	25.49	−0.4180	0.8965	0.5483	24.22	−0.1361
0.5425	0.9288	0.7408	26.46	−0.3430	0.9181	0.6404	25.23	−0.3583	0.9075	0.5992	24.01	0.0273
0.6401	0.9403	0.7985	26.17	−0.2711	0.9295	0.6944	24.97	−0.2530	0.9189	0.6572	23.81	0.2271
0.7345	0.9520	0.8638	25.89	−0.1764	0.9413	0.7553	24.73	−0.1171	0.9307	0.7128	23.62	0.4525
0.8181	0.9629	0.9242	25.65	−0.0772	0.9522	0.8095	24.52	0.0241	0.9416	0.7516	23.45	0.6797
0.9143	0.9761	0.9886	25.37	0.0556	0.9654	0.8616	24.27	0.2091	0.9547	0.7697	23.27	1.0053
1.0000	0.9882	1.0305	25.13	—	0.9774	0.8858	24.07	—	0.9666	0.7412	23.10	—
(c) System: butanoic acid (1) + benzene (2)												
Temp.	$T = 298.15, \text{ K}$				$T = 308.15, \text{ K}$				$T = 318.15, \text{ K}$			
x_1	$10^{-3} \rho,$ kg m^{-3}	$\eta, \text{ mPa s}$	$10^3 \sigma,$ N m^{-1}	d	$10^{-3} \rho,$ kg m^{-3}	$\eta, \text{ mPa s}$	$10^3 \sigma,$ N m^{-1}	d	$10^{-3} \rho,$ kg m^{-3}	$\eta, \text{ mPa s}$	$10^3 \sigma,$ N m^{-1}	d
0.0000	0.8782	0.6035	28.21	—	0.8669	0.5294	26.75	—	0.8560	0.4588	25.24	—
0.0965	0.8844	0.6554	27.84	−0.0821	0.8737	0.5723	26.43	−0.0502	0.8629	0.4944	24.99	0.0442
0.1938	0.8909	0.7002	27.52	−0.2023	0.8806	0.6046	26.16	−0.2071	0.8699	0.5501	24.77	0.2503
0.2918	0.8978	0.7427	27.20	−0.3081	0.8877	0.6437	25.89	−0.2583	0.8772	0.6162	24.56	0.3907
0.3906	0.9049	0.7987	26.91	−0.3482	0.8949	0.6954	25.65	−0.2540	0.8846	0.6849	24.37	0.4783
0.4902	0.9124	0.8763	26.63	−0.3304	0.9026	0.7645	25.42	−0.2031	0.8923	0.7501	24.19	0.5266
0.5906	0.9202	0.9788	26.35	−0.2691	0.9105	0.8516	25.20	−0.1171	0.9003	0.8078	24.01	0.460
0.6917	0.9279	1.1049	26.08	−0.1782	0.9186	0.9534	24.97	−0.0074	0.9085	0.8558	23.84	0.5413
0.7937	0.9360	1.2480	25.81	−0.0671	0.9268	1.0620	24.75	0.1182	0.9169	0.8944	23.67	0.5170
0.8964	0.9444	1.3954	25.55	0.0573	0.9351	1.1645	24.53	0.2564	0.9253	0.9262	23.51	0.4754
1.0000	0.9533	1.5283	25.31	—	0.9434	1.2421	24.33	—	0.9335	0.9562	23.35	—

(d) System: ethanoic acid (1) + acetophenone (2)

Temp.	$T = 298.15, \text{ K}$				$T = 308.15, \text{ K}$				$T = 318.15, \text{ K}$			
x_1	$10^{-3} \rho, \text{ kg m}^{-3}$	$\eta, \text{ mPa s}$	$10^3 \sigma, \text{ N m}^{-1}$	d	$10^{-3} \rho, \text{ kg m}^{-3}$	$\eta, \text{ mPa s}$	$10^3 \sigma, \text{ N m}^{-1}$	d	$10^{-3} \rho, \text{ kg m}^{-3}$	$\eta, \text{ mPa s}$	$10^3 \sigma, \text{ N m}^{-1}$	d
0.0000	1.0241	1.6589	38.74	—	1.0156	1.3469	37.67	—	1.0069	1.0082	36.28	—
0.1852	1.0279	1.6468	36.98	0.4216	1.0196	1.3674	36.12	0.5305	1.0113	1.0954	34.92	0.8861
0.3384	1.0309	1.6127	35.53	0.4529	1.0228	1.3692	34.57	0.6030	1.0139	1.1265	33.59	0.9093
0.4672	1.0334	1.5613	34.19	0.4753	1.0250	1.3465	33.14	0.6565	1.0161	1.1242	32.27	0.9515
0.5770	1.0357	1.4993	32.83	0.4912	1.0269	1.3048	31.84	0.6984	1.0179	1.1006	31.00	1.0064
0.6717	1.0374	1.4329	31.62	0.5028	1.0284	1.2511	30.66	0.7329	1.0192	1.0622	29.77	1.0707
0.7542	1.0393	1.3662	30.55	0.5111	1.0299	1.1908	29.60	0.7616	1.0205	1.0136	28.59	1.1427
0.8268	1.0406	1.3014	29.41	0.5166	1.0306	1.1282	28.63	0.7860	1.0215	0.9577	27.68	1.2224
0.8911	1.0419	1.2403	28.52	0.5206	1.0317	1.0659	27.76	0.8071	1.0221	0.8969	26.74	1.3091
0.9485	1.0432	1.1834	27.81	0.5239	1.0324	1.0057	26.96	0.8245	1.0217	0.8328	25.95	1.4040
1.0000	1.0437	1.1310	27.10	—	1.0325	0.9487	26.10	—	1.0213	0.7667	25.11	—

(e) System: propanoic acid (1) + acetophenone (2)

Temp.	$T = 298.15, \text{ K}$				$T = 308.15, \text{ K}$				$T = 318.15, \text{ K}$			
x_1	$10^{-3} \rho, \text{ kg m}^{-3}$	$\eta, \text{ mPa s}$	$10^3 \sigma, \text{ N m}^{-1}$	d	$10^{-3} \rho, \text{ kg m}^{-3}$	$\eta, \text{ mPa s}$	$10^3 \sigma, \text{ N m}^{-1}$	d	$10^{-3} \rho, \text{ kg m}^{-3}$	$\eta, \text{ mPa s}$	$10^3 \sigma, \text{ N m}^{-1}$	d
0.0000	1.0241	1.6589	38.74	—	1.0156	1.3469	37.67	—	1.0069	1.0082	36.28	—
0.1485	1.0234	1.6616	37.55	0.5718	1.0155	1.4078	36.60	0.8421	1.0071	1.1222	35.46	1.2083
0.2818	1.0211	1.6244	35.95	0.5591	1.0132	1.4109	35.05	0.8131	1.0047	1.1734	33.93	1.1780
0.4022	1.0184	1.5657	34.23	0.5559	1.0102	1.3815	33.32	0.8065	1.0016	1.1826	32.18	1.1781
0.5113	1.0155	1.4956	32.61	0.5594	1.0070	1.3330	31.60	0.8161	0.9982	1.1627	30.45	1.2000
0.6108	1.0123	1.4199	30.97	0.5689	1.0036	1.2730	29.94	0.8395	0.9947	1.1217	28.82	1.2302
0.7019	1.0087	1.3417	29.52	0.5831	0.9999	1.2053	28.48	0.8748	0.9908	1.0651	27.40	1.2044
0.7855	1.0046	1.2630	28.20	0.6014	0.9956	1.1318	27.23	0.9211	0.9862	0.9965	26.22	1.3648
0.8626	0.9999	1.1846	27.10	0.6236	0.9905	1.0538	26.05	0.9795	0.9808	0.9184	25.14	1.4520
0.9339	0.9945	1.1069	26.09	0.6494	0.9845	0.9718	25.05	1.0520	0.9743	0.8326	24.13	1.5548
1.0000	0.9882	1.0305	25.13	—	0.9774	0.8858	24.07	—	0.9666	0.7412	23.10	—

(f) System: butanoic acid (1) + acetophenone (2)

Temp.	$T = 298.15, \text{ K}$				$T = 308.15, \text{ K}$				$T = 318.15, \text{ K}$			
x_1	$10^{-3} \rho, \text{ kg m}^{-3}$	$\eta, \text{ mPa s}$	$10^3 \sigma, \text{ N m}^{-1}$	d	$10^{-3} \rho, \text{ kg m}^{-3}$	$\eta, \text{ mPa s}$	$10^3 \sigma, \text{ N m}^{-1}$	d	$10^{-3} \rho, \text{ kg m}^{-3}$	$\eta, \text{ mPa s}$	$10^3 \sigma, \text{ N m}^{-1}$	d
0.0000	1.0241	1.6589	38.74	—	1.0156	1.3469	37.67	—	1.0069	1.0082	36.28	—
0.1238	1.0192	1.6809	37.21	0.2147	1.0114	1.4359	36.20	0.6827	1.0029	1.1843	34.89	1.5446
0.2412	1.0135	1.6949	35.81	0.2254	1.0057	1.4832	34.82	0.6336	0.9975	1.2710	33.55	1.3354
0.3528	1.0073	1.6994	34.47	0.2323	0.9993	1.5199	33.48	0.6545	0.9912	1.3134	32.28	1.2401
0.4588	1.0007	1.6943	33.19	0.2364	0.9925	1.5224	32.20	0.6429	0.9844	1.3145	31.04	1.1663
0.5598	0.9937	1.6803	31.90	0.2382	0.9855	1.5164	30.93	0.6650	0.9772	1.2913	29.83	1.1244
0.6561	0.9864	1.6587	30.63	0.2379	0.9781	1.4854	29.67	0.6693	0.9696	1.2499	28.60	1.1067
0.7480	0.9788	1.6311	29.36	0.2358	0.9703	1.4423	28.40	0.6845	0.9616	1.1897	27.34	1.0885
0.8357	0.9708	1.5991	28.08	0.2318	0.9621	1.3868	27.13	0.7058	0.9529	1.1232	26.10	1.1087
0.9197	0.9623	1.5644	26.79	0.2269	0.9531	1.3154	25.81	0.6884	0.9436	1.0526	24.80	1.2427
1.0000	0.9533	1.5283	25.31	—	0.9434	1.2421	24.33	—	0.9335	0.9562	23.35	—

TABLE 3: Coefficients and standard deviation (SD) of (3).

(a) System: ethanoic acid (1) + benzene (2)							
Property	a_0	a_1	b_0	b_1	b_2	b_3	SD
$10^{-3} \rho$, kg m $^{-3}$	0.0119	-0.0023	127.7241	25.6751	1.5885	26.0451	0.0005
η , mPa s	59.5012	-0.0292	38.0928	15.3389	-91.5172	162.0792	0.0098
$10^3 \sigma$, N m $^{-1}$	152.321	-0.0092	78.8979	-6.4061	5.4754	-3.1067	0.0787
(b) System: propanoic acid (1) + benzene (2)							
Property	a_0	a_1	b_0	b_1	b_2	b_3	SD
$10^{-3} \rho$, kg m $^{-3}$	0.0646	-0.0023	23.8828	4.1347	2.0768	0.2422	0.0004
η , mPa s	8.5892	-0.0253	84.0671	-51.2057	289.9852	-91.7128	0.0121
$10^3 \sigma$, N m $^{-1}$	67.3803	-0.0098	218.9691	-50.9015	14.4385	-5.0172	0.0531
(c) System: butanoic acid (1) + benzene (2)							
Property	a_0	a_1	b_0	b_1	b_2	b_3	SD
$10^{-3} \rho$, kg m $^{-3}$	0.0075	-0.0022	197.7351	31.0052	5.3648	0.0082	0.0004
η , mPa s	1.1224	-0.0039	0.9317	0.9135	1.0511	0.9013	0.1174
$10^3 \sigma$, N m $^{-1}$	40.7458	-0.0097	345.5491	-83.2693	35.6763	-12.5341	0.0789
(d) System: ethanoic acid (1) + acetophenone (2)							
Property	a_0	a_1	b_0	b_1	b_2	b_3	SD
$10^{-3} \rho$, kg m $^{-3}$	0.0133	-0.0018	135.4120	5.3912	0.5035	-1.2567	0.0008
η , mPa s	5.5360	-0.0078	1.0852	0.8055	0.1232	0.6509	0.3807
$10^3 \sigma$, N m $^{-1}$	19.8974	-0.0061	466.4421	-181.1751	-103.1812	43.4471	0.0814
(e) System: propanoic acid (1) + acetophenone (2)							
Property	a_0	a_1	b_0	b_1	b_2	b_3	SD
$10^{-3} \rho$, kg m $^{-3}$	0.0247	-0.0018	72.3523	-1.2922	-0.0496	-3.9453	0.0011
η , mPa s	478.863	-0.0308	51.9435	32.5293	-96.0902	33.3408	0.0217
$10^3 \sigma$, N m $^{-1}$	82.6053	-0.0066	129.2180	-39.9785	-99.9945	64.4734	0.0998
(f) System: butanoic acid (1) + acetophenone (2)							
Property	a_0	a_1	b_0	b_1	b_2	b_3	SD
$10^{-3} \rho$, kg m $^{-3}$	0.0219	-0.0017	80.5712	-5.6413	-4.3236	-1.0553	0.0005
η , mPa s	406.2351	-0.0313	70.2532	69.7560	-96.7418	16.7550	0.0271
$10^3 \sigma$, N m $^{-1}$	71.4271	-0.0067	156.1280	-99.6785	26.3214	-17.0516	0.0658

these parameters along with standard deviation is reported in Table 4. Consider

$$SD = \sqrt{\frac{\sum (\text{observed} - \text{calculated})^2}{N - 1}}, \quad (10)$$

where N is the total number of experimental points.

Stevanovic et al. [14] have recently compared the available correlation models for liquid mixture viscosities of organic compounds. Amongst the available correlations for predicting the binary liquid mixture viscosity, the present experimental binary viscosity data was fitted to the following five correlations.

McAllister's [15] model:

$$\ln \eta_{\text{mix}} = x_1^3 \ln \eta_1 + x_2^3 \ln \eta_2 + 3x_1^2 x_2 \ln \eta_{12} + 3x_1 x_2^2 \ln \eta_{21}$$

$$\begin{aligned} & - \ln \left[x_1 + x_2^2 \left(\frac{M_2}{M_1} \right) \right] + x_1^2 x_2 \ln \left[\frac{2}{3} + \left(\frac{M_2}{3M_1} \right) \right] \\ & + 3x_1 x_2^2 \ln \left[\frac{1}{3} + \left(\frac{2M_2}{3M_1} \right) \right] + x_2^3 \ln \left(\frac{M_2}{M_1} \right), \end{aligned} \quad (11)$$

where η_{12} and η_{21} are interaction parameters.

Heric [16] model:

$$\begin{aligned} \ln \eta_{\text{mix}} = & x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 \ln M_1 \\ & + x_2 \ln M_2 - \ln (x_1 \ln M_1 + x_1 \ln M_2) + \beta_{12}, \end{aligned} \quad (12)$$

where β_{12} is a deviation function given by

$$\beta_{12} = x_1 x_2 [\delta_{12} + \delta_{21} (x_1 - x_2)]. \quad (13)$$

Here, δ_{12} and δ_{21} are interaction parameters.

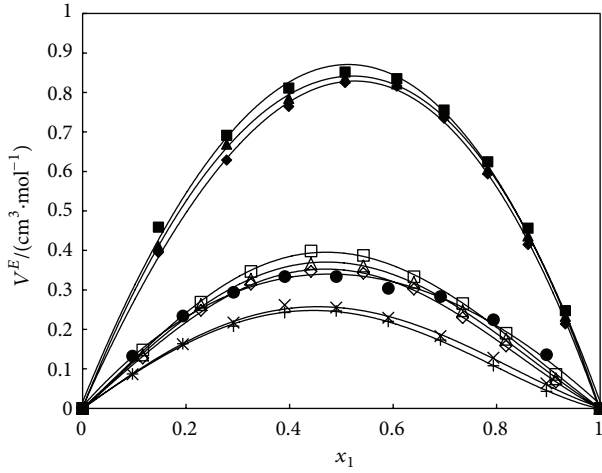


FIGURE 1: Plot of V^E versus x_1 for EA + BEN (■ 298.15 K, ▲ 308.15 K, ◆ 318.15 K); PA + BEN (□ 298.15 K, △ 308.15 K, ◇ 318.15 K); II BA+BEN (● 298.15 K, × 308.15 K, + 318.15 K) III calculated from (5).

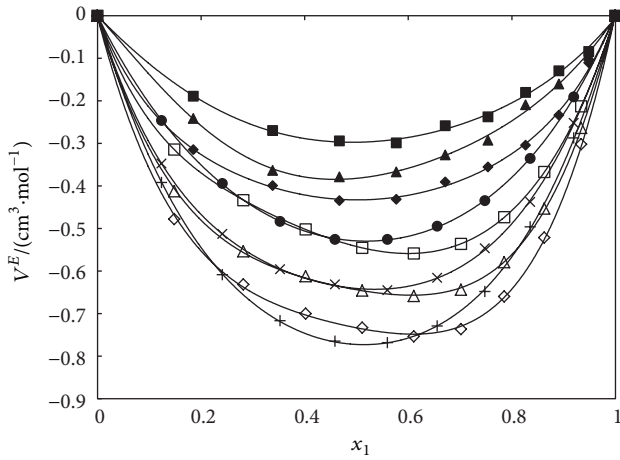


FIGURE 2: Plot of V^E versus x_1 for EA + ACT (■ 298.15 K, ▲ 308.15 K, ◆ 318.15 K) IV; PA + ACT (□ 298.15 K, △ 308.15 K, ◇ 318.15 K) V; BA + ACT (● 298.15 K, × 308.15 K, + 318.15 K) VI calculated from (5).

Auslander [17] model:

$$x_1 (x_1 + B_{12}x_2) (\eta_{\text{mix}} - \eta_1) + A_{21}x_2 (B_{21}x_1 + x_2) (\eta_{\text{mix}} - \eta_2) = 0, \quad (14)$$

where B_{12} , A_{21} , and B_{21} are parameters representing binary interactions.

Teja and Rice [18] model:

$$\ln(\eta_{\text{mix}}\varepsilon_{\text{mix}}) = x_1 \ln(\eta_1\varepsilon_1) + x_2 \ln(\eta_2\varepsilon_2), \quad (15)$$

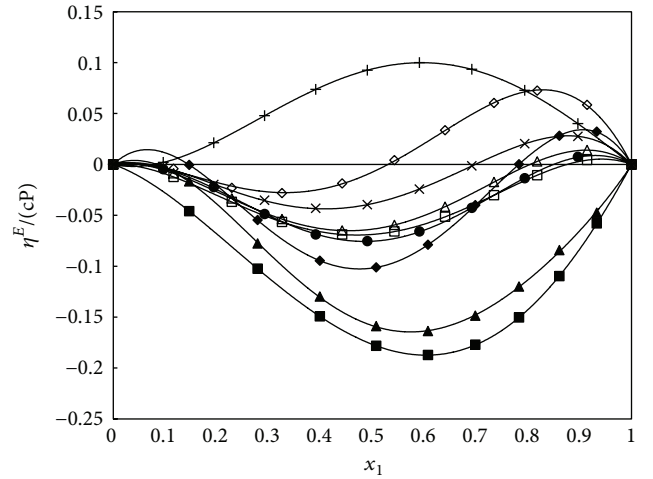


FIGURE 3: Plot of η^E versus x_1 for EA + BEN (■ 298.15 K, ▲ 308.15 K, ◆ 318.15 K) I; PA + BEN (□ 298.15 K, △ 308.15 K, ◇ 318.15 K) II; BA + BEN (● 298.15 K, × 308.15 K, + 318.15 K) III calculated from (6).

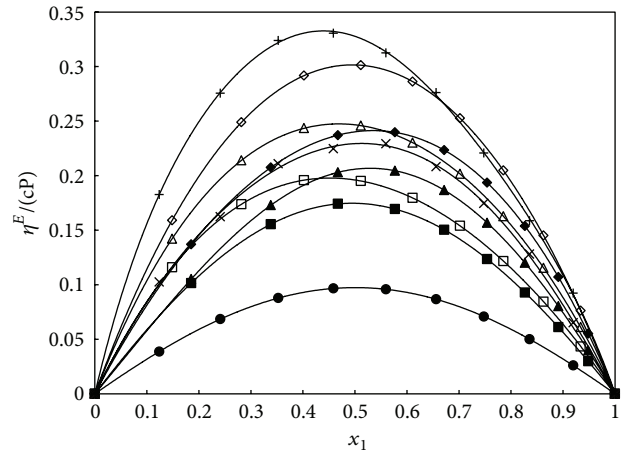


FIGURE 4: Plot of η^E versus x_1 for EA + ACT (■ 298.15 K, ▲ 308.15 K, ◆ 318.15 K) IV; PA + ACT (□ 298.15 K, △ 308.15 K, ◇ 318.15 K) V; BA + ACT (● 298.15 K, × 308.15 K, + 318.15 K) VI calculated from (6).

where $\varepsilon_i = V_{ci}^{2/3}/(T_{ci}M_i)^{1/2}$ for $i = 1$ or 2 component or the mixture

$$V_{\text{cmix}} = \frac{1}{8} [x_1^2 V_{C1} + x_2^2 V_{C2} + 2x_1x_2 (V_{C1}^{1/3} + V_{C2}^{1/3})],$$

$$T_{\text{cmix}} = \frac{1}{V_{\text{cmix}}} [x_1^2 T_{c1} V_{c1} + x_2^2 T_{c2} V_{c2} + 2x_1x_2 \varphi_{12} (T_{c1} V_{c1} T_{c2} V_{c2})^{1/2}]; \quad (16)$$

η_1 must be evaluated at a temperature $T(T_{c1}/T_{\text{cmix}})$ and η_2 at a temperature $T(T_{c2}/T_{\text{cmix}})$. T is the system temperature and φ_{12} is an adjustable interaction parameter having a value unity. The interaction parameter has been shown to be

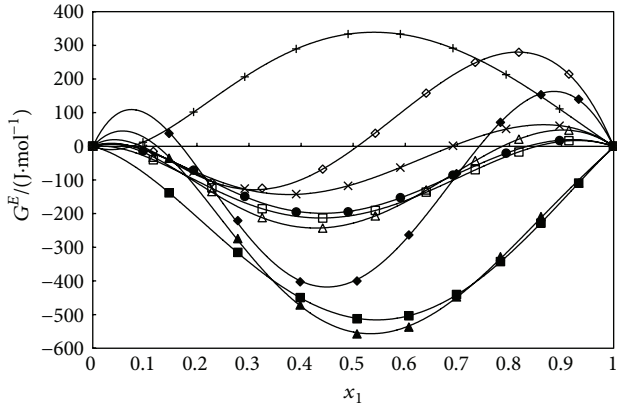


FIGURE 5: Plot of G^E versus x_1 for EA + BEN (■ 298.15 K, ▲ 308.15 K, ◆ 318.15 K) I; PA + BEN (□ 298.15 K, △ 308.15 K, ◇ 318.15 K) II; BA + BEN (● 298.15 K, × 308.15 K, + 318.15 K) III calculated from (7).

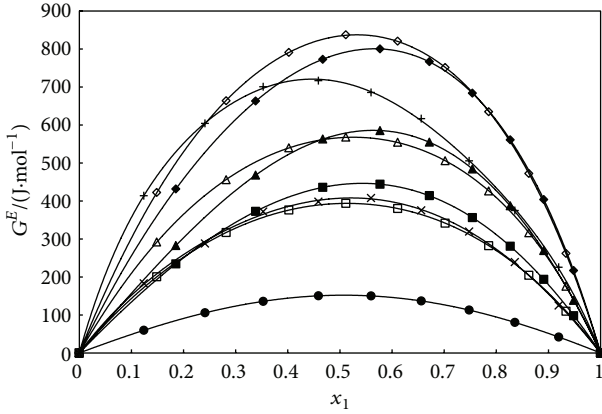


FIGURE 6: Plot of G^E versus x_1 for EA + ACT (■ 298.15 K, ▲ 308.15 K, ◆ 318.15 K) IV; PA + ACT (□ 298.15 K, △ 308.15 K, ◇ 318.15 K) V; BA + ACT (● 298.15 K, × 308.15 K, + 318.15 K) VI calculated from (7).

independent of temperature and composition [19, 20]. The subscript c indicates a reduced quantity.

Kubendran et al. model [21]:

$$\begin{aligned} \ln \eta_{\text{mix}} &= x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 \ln M_1 \\ &+ x_2 \ln M_2 - \ln [x_1 M_1 + x_2 M_2] \\ &- 2.303 x_1 x_2 [B_{12} + C_{12} (x_1 - x_2) + D_{12} (x_1 - x_2)^2], \end{aligned} \quad (17)$$

where B_{12} , C_{12} , and D_{12} are binary interaction constants.

The observed data on surface tension of binary mixtures was fitted to the following models available in the literature.

Zihao and Jufu model [22]:

$$\sigma_{\text{mix}} = \frac{x_1 \sigma_1}{x_1 + \gamma_{12} x_2} + \frac{x_2 \sigma_2}{x_2 + \gamma_{21} x_1}, \quad (18)$$

where γ_{12} and γ_{21} are interaction parameters.

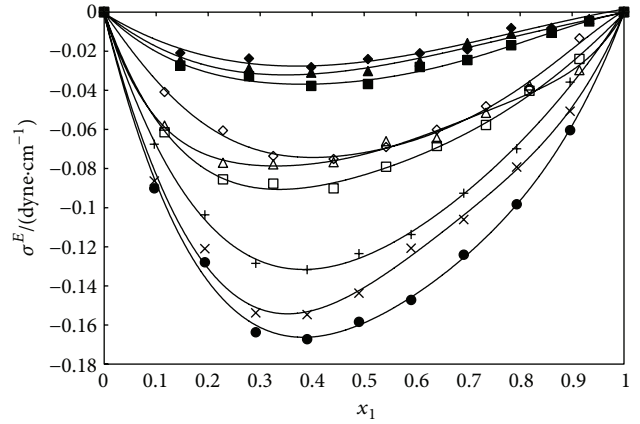


FIGURE 7: Plot of σ^E versus x_1 for EA + BEN (■ 298.15 K, ▲ 308.15 K, ◆ 318.15 K) I; PA + BEN (□ 298.15 K, △ 308.15 K, ◇ 318.15 K) V; BA + BEN (● 298.15 K, × 308.15 K, + 318.15 K) VI calculated from (8).

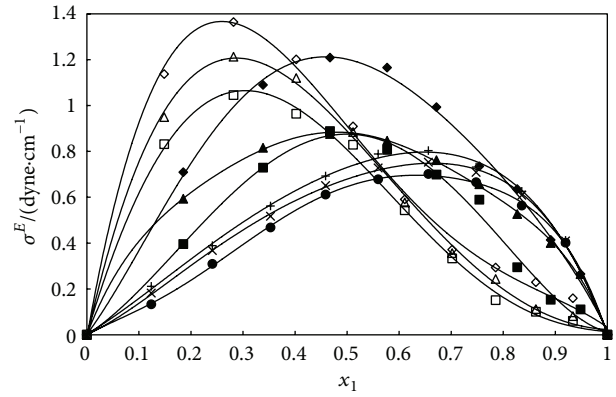


FIGURE 8: Plot of σ^E versus x_1 for EA + ACT (■ 298.15 K, ▲ 308.15 K, ◆ 318.15 K) I; PA + ACT (□ 298.15 K, △ 308.15 K, ◇ 318.15 K) V; BA + ACT (● 298.15 K, × 308.15 K, + 318.15 K) VI calculated from (8).

Rice and Teja model [23]:

$$\frac{\sigma_{\text{mix}}}{\Phi_{\text{mix}}} = x_1 \sigma_1 \Phi_1 + x_2 \sigma_2 \Phi_2, \quad (19)$$

where $\Phi_i = V_{ci}^{2/3} / T_{ci}$ for $i = 1$ or 2 component or the mixture

$$\begin{aligned} V_{\text{cmix}} &= \frac{1}{8} [x_1^2 V_{C1} + x_2^2 V_{C2} + 2x_1 x_2 (V_{C1}^{1/3} + V_{C2}^{1/3})], \\ T_{\text{cmix}} &= \frac{1}{V_{\text{cmix}}} [x_1^2 T_{c1} V_{c1} + x_2^2 T_{c2} V_{c2} \\ &+ 2x_1 x_2 \varphi_{12} (T_{c1} V_{c1} T_{c2} V_{c2})^{1/2}]. \end{aligned} \quad (20)$$

Here, σ_1 is to be evaluated at a temperature $= T (T_{c1} / T_{\text{cmix}})$ and σ_2 at a temperature $= T (T_{c2} / T_{\text{cmix}})$. T is the system temperature and φ_{12} is an adjustable interaction parameter having a value around unity. The interaction parameter has been shown to be independent of temperature and composition [19, 20]. The subscript c indicates a reduced quantity.

TABLE 4: Coefficients of (9) and standard deviation (SD) determined by the method of least squares.

(a) System: ethanoic acid (1) + benzene (2)												
Temp.	$T = 298.15, \text{ K}$				$T = 308.15, \text{ K}$				$T = 318.15, \text{ K}$			
Coeff. of (9)	$V^E, \text{ cm}^3 \text{ mol}^{-1}$	$G^E, \text{ J mol}^{-1}$	$\eta^E, \text{ mPa s}$	$\sigma^E, \text{ dyne cm}^{-1}$	$V^E, \text{ cm}^3 \text{ mol}^{-1}$	$G^E, \text{ J mol}^{-1}$	$\eta^E, \text{ mPa s}$	$\sigma^E, \text{ dyne cm}^{-1}$	$V^E, \text{ cm}^3 \text{ mol}^{-1}$	$G^E, \text{ J mol}^{-1}$	$\eta^E, \text{ mPa s}$	$\sigma^E, \text{ dyne cm}^{-1}$
A_0	3.4057	-2036.7	-0.7083	-0.1438	3.3546	-2190.4	-0.6270	-0.1148	3.2885	-1582.1	-0.4091	-0.1021
A_1	0.1473	-570.94	-0.3870	0.1166	0.2460	-919.75	-0.3834	0.0811	0.3229	875.912	0.1482	0.0671
A_2	0.5936	1060.26	0.1385	0.0069	0.2239	2253.75	0.3941	-0.0229	0.0329	4602.96	1.0281	0.0052
SD	0.0046	0.9097	0.0004	0.0024	0.0066	15.0513	0.0029	0.0019	0.0106	20.9443	0.0006	0.0025
(b) System: propanoic acid (1) + benzene (2)												
Temp.	$T = 298.15, \text{ K}$				$T = 308.15, \text{ K}$				$T = 318.15, \text{ K}$			
Coeff. of (9)	$V^E, \text{ cm}^3 \text{ mol}^{-1}$	$G^E, \text{ J mol}^{-1}$	$\eta^E, \text{ mPa s}$	$\sigma^E, \text{ dyne cm}^{-1}$	$V^E, \text{ cm}^3 \text{ mol}^{-1}$	$G^E, \text{ J mol}^{-1}$	$\eta^E, \text{ mPa s}$	$\sigma^E, \text{ dyne cm}^{-1}$	$V^E, \text{ cm}^3 \text{ mol}^{-1}$	$G^E, \text{ J mol}^{-1}$	$\eta^E, \text{ mPa s}$	$\sigma^E, \text{ dyne cm}^{-1}$
A_0	1.5593	-817.53	-0.2753	-0.3333	1.4645	-908.81	-0.2545	-0.2841	1.3824	-59.558	-0.0305	-0.2906
A_1	-0.1945	406.993	0.0821	0.1821	-0.2298	631.847	0.1348	0.1516	-0.2524	1926.95	0.4671	0.1026
A_2	-0.5306	1137.63	0.3751	-0.1745	-0.4702	1653.71	0.4651	-0.2454	-0.4703	1900.34	0.5546	-0.0278
SD	0.0025	4.9749	0.0002	0.0022	0.0033	7.6158	0.0001	0.0032	0.0035	13.9527	0.0011	0.0023
(c) System: butanoic acid (1) + benzene (2)												
Temp.	$T = 298.15, \text{ K}$				$T = 308.15, \text{ K}$				$T = 318.15, \text{ K}$			
Coeff. of (9)	$V^E, \text{ cm}^3 \text{ mol}^{-1}$	$G^E, \text{ J mol}^{-1}$	$\eta^E, \text{ mPa s}$	$\sigma^E, \text{ dyne cm}^{-1}$	$V^E, \text{ cm}^3 \text{ mol}^{-1}$	$G^E, \text{ J mol}^{-1}$	$\eta^E, \text{ mPa s}$	$\sigma^E, \text{ dyne cm}^{-1}$	$V^E, \text{ cm}^3 \text{ mol}^{-1}$	$G^E, \text{ J mol}^{-1}$	$\eta^E, \text{ mPa s}$	$\sigma^E, \text{ dyne cm}^{-1}$
A_0	1.3265	-766.41	-0.2993	-0.6355	0.9972	-479.11	-0.1557	-0.5632	0.9699	1437.98	0.3753	-0.4996
A_1	-0.0839	352.158	0.0682	0.2170	-0.2319	723.101	0.2175	0.2762	-0.2740	538.149	0.2511	0.2161
A_2	0.2549	1271.88	0.5053	-0.2678	-0.2829	1144.88	0.4437	-0.2589	-0.4747	-1097.5	-0.2301	-0.1274
SD	0.0025	7.9049	0.0011	0.0037	0.0026	10.4486	0.0005	0.0045	0.0011	7.4136	0.0001	0.0019
(d) System: ethanoic acid (1) + acetophenone (2)												
Temp.	$T = 298.15, \text{ K}$				$T = 308.15, \text{ K}$				$T = 318.15, \text{ K}$			
Coeff. of (9)	$V^E, \text{ cm}^3 \text{ mol}^{-1}$	$G^E, \text{ J mol}^{-1}$	$\eta^E, \text{ mPa s}$	$\sigma^E, \text{ dyne cm}^{-1}$	$V^E, \text{ cm}^3 \text{ mol}^{-1}$	$G^E, \text{ J mol}^{-1}$	$\eta^E, \text{ mPa s}$	$\sigma^E, \text{ dyne cm}^{-1}$	$V^E, \text{ cm}^3 \text{ mol}^{-1}$	$G^E, \text{ J mol}^{-1}$	$\eta^E, \text{ mPa s}$	$\sigma^E, \text{ dyne cm}^{-1}$
A_0	-1.1887	1773.18	0.6988	3.5069	-1.5271	2302.41	0.8237	3.4363	-1.7228	3144.69	0.9608	4.7515
A_1	-0.0156	318.334	-0.0168	-0.1138	0.0861	643.012	0.1139	-0.1918	0.0136	795.337	0.1274	-0.4302
A_2	-0.2739	-46.906	-0.0924	-2.4741	-0.2552	-51.471	-0.1390	1.1646	-0.9039	600.09	0.0699	0.4843
SD	0.0078	0.2584	0.0001	0.0368	0.0107	0.5067	0.0001	0.0249	0.0077	2.8808	0.0001	0.0421
(e) System: propanoic acid (1) + acetophenone (2)												
Temp.	$T = 298.15, \text{ K}$				$T = 308.15, \text{ K}$				$T = 318.15, \text{ K}$			
Coeff. of (9)	$V^E, \text{ cm}^3 \text{ mol}^{-1}$	$G^E, \text{ J mol}^{-1}$	$\eta^E, \text{ mPa s}$	$\sigma^E, \text{ dyne cm}^{-1}$	$V^E, \text{ cm}^3 \text{ mol}^{-1}$	$G^E, \text{ J mol}^{-1}$	$\eta^E, \text{ mPa s}$	$\sigma^E, \text{ dyne cm}^{-1}$	$V^E, \text{ cm}^3 \text{ mol}^{-1}$	$G^E, \text{ J mol}^{-1}$	$\eta^E, \text{ mPa s}$	$\sigma^E, \text{ dyne cm}^{-1}$
A_0	-2.1586	1575.04	0.7842	3.2115	-2.5740	2266.12	0.9866	3.5476	-2.9319	3336.55	1.2061	3.6371
A_1	-0.4770	89.9121	-0.1441	-4.1671	-0.4158	224.961	-0.1081	-4.8025	-0.4622	412.138	-0.0243	-5.4345
A_2	-1.1862	159.141	0.0621	0.8986	-1.8773	440.569	0.1263	1.6488	-2.9319	636.631	0.0692	3.7051
SD	0.0057	0.4763	0.0001	0.0296	0.0046	1.7711	0.0001	0.0289	-0.4622	2.5552	0.0001	0.0371
(f) System: butanoic acid (1) + acetophenone (2)												
Temp.	$T = 298.15, \text{ K}$				$T = 308.15, \text{ K}$				$T = 318.15, \text{ K}$			
Coeff. of (9)	$V^E, \text{ cm}^3 \text{ mol}^{-1}$	$G^E, \text{ J mol}^{-1}$	$\eta^E, \text{ mPa s}$	$\sigma^E, \text{ dyne cm}^{-1}$	$V^E, \text{ cm}^3 \text{ mol}^{-1}$	$G^E, \text{ J mol}^{-1}$	$\eta^E, \text{ mPa s}$	$\sigma^E, \text{ dyne cm}^{-1}$	$V^E, \text{ cm}^3 \text{ mol}^{-1}$	$G^E, \text{ J mol}^{-1}$	$\eta^E, \text{ mPa s}$	$\sigma^E, \text{ dyne cm}^{-1}$
A_0	-2.1062	609.099	0.3895	2.5197	-2.5541	1683.49	0.9184	2.7061	-3.0827	3014.95	1.2999	2.9131
A_1	-0.1445	19.8592	0.0009	1.9580	-0.1158	82.0211	0.0129	1.8902	-0.1071	-644.28	-0.3272	1.8747

(f) Continued.

Temp.	$T = 298.15, \text{ K}$				$T = 308.15, \text{ K}$				$T = 318.15, \text{ K}$			
Coeff. of (9)	$V^E, \text{ cm}^3 \text{ mol}^{-1}$	$G^E, \text{ J mol}^{-1}$	$\eta^E, \text{ mPa s}$	$\sigma^E, \text{ dyne cm}^{-1}$	$V^E, \text{ cm}^3 \text{ mol}^{-1}$	$G^E, \text{ J mol}^{-1}$	$\eta^E, \text{ mPa s}$	$\sigma^E, \text{ dyne cm}^{-1}$	$V^E, \text{ cm}^3 \text{ mol}^{-1}$	$G^E, \text{ J mol}^{-1}$	$\eta^E, \text{ mPa s}$	$\sigma^E, \text{ dyne cm}^{-1}$
A_2	-0.4769	-78.407	-0.0556	0.6841	-1.1813	104.424	-0.0028	0.9832	-1.0573	860.142	0.2081	0.8359
SD	0.0019	0.0827	0.0001	0.0267	0.0049	5.0118	0.0029	0.0194	0.0031	8.1692	0.0031	0.0183

Empirical two-constant model [24]:

$$\sigma_{\text{mix}} = x_1\sigma_1 + x_2\sigma_2 + x_1x_2[A' + B'(x_1 - x_2)], \quad (21)$$

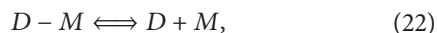
where A' and B' are binary interaction parameters.

The model parameters of (11), and (13)–(21) were determined using nonlinear regression technique and the estimated values are reported in Table 5.

4. Discussion

The values of V^E as illustrated in Figures 1 and 2 are positive for the entire concentration range at all the three temperatures for the systems EA + BEN, PA + BEN, and BA + BEN and negative for the remaining three systems. About 5% more negative or less positive V^E values at higher temperatures for all the systems may be due to increased population of acid monomers to enter into the hetero-intermolecular interactions.

The positive and negative V^E values may be explained by considering the following three steps equilibria accompanying the mixing process as proposed by Lark and Banipal [2]:



where D and M denote a dimer and a monomer of the acid under question. The first process is accompanied with a large volume increase in the right direction; the second is isochoric; that is, the volume of the dimer is assumed to be equal to twice the value of the monomer [4, 5]; the third step is accompanied with large contraction in case of ACT and expansion in case of BEN. So the addition of ACT or BEN to anyone of the acids first creates monomers by the first two steps resulting in expansion. In the third step, stronger heteromolecular dipole-dipole interactions result in the observed negative V^E in case of CA + ACT and positive V^E values in the case of CA + BEN system due to induced dipole-dipole interactions. Therefore, the third step is accompanied with contraction in volume in case of ACT and expansion in case of BEN.

The pK_a values of EA, PA, and BA are 4.76, 4.88, and 4.82, respectively. It is expected that the order of dimerization constants of various acids would increase in the same order. The increasing dimerization constant would lead to a smaller number of available monomers and thus to a smaller volume increase as described by (22).

However, the observed order of V^E for the CA + BEN system is as follows: BA > PA > EA (Table 6). This shows that in case of BEN there are strong acid-solvent interactions which govern the magnitude and sign of V^E , which increases as the inductive effect of alkyl chain of the acid as is also observed by Lark et al. [25]. Similar results were also obtained by Venkateswarlu and Raman [26] as the positive excess volumes of 1,2-dichloroethane and 1,2-dibromoethane with three acids observe the following order: BA > PA > EA, which is the same as discussed above; that is, the increase in chain length of acid contributes to the decrease in excess volume. The large negative V^E values in the case of CA + ACT mixture arise due to depolymerization of acid accompanied with strong hydrogen-bonded heterocomplex formation. However, in CA + ACT system, the V^E values follow the order PA > BA > EA as was also observed by Lark et al. [25] in CA + MEOH system.

The data presented in Figures 3 and 4 reveal that excess viscosity (η^E) is positive for the systems EA + ACT, PA + ACT, and BA + ACT, and is negative for the systems EA + BEN, PA + BEN, and BA + BEN at 298.15 K. The algebraic positive values of η^E may be represented in the following order: PA + ACT > EA + ACT > BA + ACT > BA + BEN > PA + BEN > EA + BEN. The sign and magnitude of η^E depend on the combined effect of the factors such as molecular size, shape, and intermolecular forces. The positive value of η^E for the CA + ACT system suggests that the viscosity of the mixture is higher than that of the pure components and hence the fluidity of the mixture is low. This indicates the presence of a specific interaction such as the formation of charge-transfer complex between unlike molecules. The negative value of η^E in the systems EA + BEN, PA + BEN, and BA + BEN suggests the mutual loss of a specific interaction in like molecules that outweigh the specific interaction between unlike molecules. The positive values of η^E increase with the increase in temperature in all these systems. The G^E values almost observe the similar trend as observed by η^E as shown in Figures 5 and 6.

The variation of Grunberg and Nissan parameter “ d ” with composition of a particular mixture is not large. The values of “ d ” are negative for CA + BEN system and positive for CA + ACT system for most of the concentration range. The positive values of “ d ” for CA + ACT system show that CA forms an intermolecular complex with ACT in the liquid phase. The values of “ d ” increase with the increase in temperature in all the systems showing that the interactions between the components increase with the increase in temperature. Even the negative values of “ d ” for CA + BEN system change

TABLE 5: Interaction parameter/parameters for various models and standard deviation (SD) determined by least square method.

(a)

Model	Constants	Ethanoic acid (1) + benzene (2)			Propanoic acid (1) + benzene (2)			Butanoic acid (1) + benzene (2)		
		298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K
McAllister (11)	η_{12}	0.6336	0.5291	0.6408	0.8286	0.7390	0.8245	1.0808	0.9825	0.9409
	η_{21}	0.5943	0.5347	0.3980	0.6163	0.5221	0.4268	0.7227	0.6129	0.6406
	SD	0.0092	0.0161	0.0289	0.0105	0.0128	0.0128	0.0146	0.0108	0.0088
	δ_{12}	-0.8692	-0.8380	-0.4591	-0.2946	-0.2916	0.0521	-0.2445	-0.1271	0.4815
Heric (13)	δ_{21}	-0.2173	-0.3069	0.4582	0.1763	0.2640	0.7480	0.1390	0.2814	0.2095
	SD	0.1357	0.2015	0.3185	0.1524	0.2269	0.3356	0.3258	0.2169	0.2614
	B_{12}	0.9275	0.9606	0.7031	0.3620	0.3859	0.0528	0.3173	0.1913	-0.5399
	C_{12}	0.2536	0.3832	-0.3062	-0.1643	-0.2472	-0.7294	-0.1430	-0.2849	-0.2063
Krishnan and Laddha (17)	D_{12}	-0.4145	-0.8715	-1.7348	-0.4654	-0.6512	-0.7241	-0.5103	-0.4499	0.4099
	SD	0.1468	0.1225	0.0701	0.0559	0.0502	0.0629	0.0595	0.0378	0.1101
	B_{12}	-0.0168	-0.0901	0.0523	1.8404	1.4898	1.9109	3.9322	2.5479	0.1292
	A_{21}	6.4585	8.2007	7.3214	6.5731	6.5502	5.6764	9.9261	6.0937	0.2803
Auslander (14)	B_{21}	0.4409	0.2966	-0.0996	0.0997	0.0271	-0.2735	0.0896	0.0999	1.7186
	SD	0.0041	0.0116	0.0121	0.0043	0.0051	0.0038	0.0074	0.0048	0.0010
Teja and Rice (15)	φ_{12}	1	1	1	1	1	1	1	1	1
	SD	0.0306	0.0224	0.0132	0.0101	0.0083	0.0131	0.0056	0.0139	0.0279
	γ_{12}	0.9377	0.9099	0.8985	0.9431	0.9413	0.9016	0.9343	0.8178	0.8038
	γ_{21}	1.0684	1.1008	1.1162	1.0624	1.0636	1.1114	1.0709	1.2259	1.2473
Zihao and Jufu (18)	SD	0.0081	0.0055	0.0049	0.0252	0.0256	0.0071	0.0858	0.0193	0.0111
	A'	0.0302	0.0304	0.0305	-0.0053	-0.0056	-0.0069	-0.0121	-0.0118	0.0079
	B'	0.0072	0.0061	0.0057	0.0061	0.0052	0.0038	0.0067	0.0096	0.0079
	SD	0.0023	0.0019	0.0024	0.0055	0.0079	0.0023	0.0088	0.0088	0.0041
Rice and Teja (19)	φ_{12}	1	1	1	1	1	1	1	1	1
	SD	0.0643	0.0128	0.0039	0.1423	0.1183	0.1183	0.2210	0.1862	0.1874

(b)

Model	Constants	Ethanoic acid (1) + acetophenone (2)			Propanoic acid (1) + acetophenone (2)			Butanoic acid (1) + acetophenone (2)		
		298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K
McAllister (11)	η_{12}	1.6072	1.4795	1.3403	1.5061	1.4196	1.3377	1.7139	1.6209	1.3511
	η_{21}	1.6910	1.4186	1.1794	1.7024	1.5097	1.3028	1.7471	1.6208	1.5934
	SD	0.0006	0.0006	0.0069	0.0034	0.0071	0.0082	0.0013	0.0034	0.0120
	δ_{12}	0.7141	0.9027	1.2314	0.6855	0.9560	1.3476	0.2817	0.7089	1.2371
Heric (13)	δ_{21}	0.1271	0.2502	0.3406	0.0584	0.1214	0.1976	0.0134	0.0417	-0.2198
	SD	0.3671	0.1578	0.2654	0.3963	0.1814	0.2120	0.6821	0.3761	0.0201
	B_{12}	-0.7161	-0.9048	-1.1986	-0.6742	-0.9286	-1.3101	-0.2854	-0.7014	-1.1893
	C_{12}	-0.1293	-0.2525	-0.3052	-0.0511	-0.1036	-0.1733	-0.0147	-0.0392	0.2360
Krishnan and Laddha (17)	D_{12}	0.0149	0.0160	-0.2399	-0.0803	-0.1955	-0.2679	0.0262	-0.0528	-0.3361
	SD	0.3071	0.3478	0.4162	0.2904	0.3731	0.4819	0.1301	0.3097	0.4936
	B_{12}	-0.0265	-0.8582	-3.1960	-0.1986	-0.9382	-3.3948	-1.9043	-7.8002	-21.0019
	A_{21}	1.5819	2.0665	1.2531	0.5603	0.6151	0.9108	1.2163	1.0309	0.5851

(b) Continued.

Model	Constants	Ethanoic acid (1) + acetophenone (2)			Propanoic acid (1) + acetophenone (2)			Butanoic acid (1) + acetophenone (2)		
		298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K
Teja and Rice (15)	B_{21}	1.2206	1.3443	4.5532	3.3567	4.7933	6.0789	2.8998	9.5205	39.1308
	SD	0.0002	0.0008	0.002	0.0002	0.0005	0.0001	0.0001	0.0026	0.0029
Teja and Rice (15)	ϕ_{12}	1.05	1.05	1.05	1.05	1.05	1.05	1.05	1.05	1.05
	SD	0.0284	0.0070	0.0146	0.0029	0.0324	0.0411	0.0826	0.0137	0.0178
Zihao and Jufu (18)	γ_{12}	0.8333	0.9319	0.8198	0.4586	0.4317	0.3288	1.2367	1.2653	1.3189
	γ_{21}	1.0468	0.9544	1.0082	1.5047	1.5256	0.4304	0.8074	0.7899	0.7593
Zihao and Jufu (18)	SD	0.0779	0.0395	0.0405	0.0474	0.0465	0.2786	0.1261	0.1209	0.1292
Two-parameter model (21)	A'	0.3968	0.4167	0.4557	0.3096	0.3329	0.3509	0.2215	0.2365	0.2478
	B'	0.0643	0.0865	0.0764	-0.0738	-0.0893	-0.1025	0.0989	0.1033	0.1075
Two-parameter model (21)	SD	0.0666	0.0599	0.0402	0.0298	0.0403	0.0983	0.0493	0.0557	0.0513
Rice and Teja (19)	ϕ_{12}	1.05	1.05	1.05	1.05	1.05	1.05	1.05	1.05	1.05
	SD	0.1802	0.1131	0.0764	0.2090	0.1756	0.1678	0.1604	0.1024	0.1126

TABLE 6: Comparison of excess volume V^E $\text{cm}^3 \text{mol}^{-1}$ of equimolar mixture at 298.15 K.

Component II	Component I		
	Ethanoic acid	Propanoic acid	Butanoic acid
Benzene	0.8514	0.3898	0.3316
Acetophenone	-0.2972	-0.5396	-0.5266

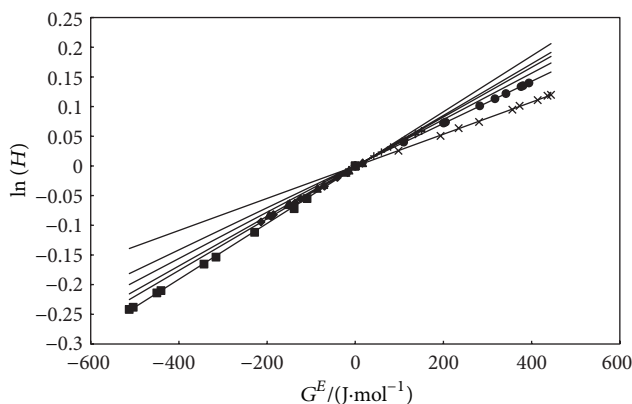


FIGURE 9: Plot of $\ln H$ versus G^E (■ EA + BEN, ◆ PA + BEN, ▲ BA + BEN, × EA + ACT, ● PA + ACT, + BA + ACT) at 298.15 K.

their sign from negative to positive with the increase in temperature from 298.15 to 318.15 K.

According to Hildebrand [27], free volume is necessary for flow and then shrinkage on mixing (which would reduce the free volume) would be associated with increase in viscosity of the system. If H is defined as η/η^o , where η is the experimental viscosity of the mixture and η^o is the ideal viscosity, calculated using

$$\eta^o = x_1 \ln \eta_1 + x_2 \ln \eta_2, \quad (25)$$

then this quantity could be related to free volume (V^o) of the solution according to Stairs [28] by the following equation:

$$H^{-1} = \frac{1}{V^o} (V^o + V^E). \quad (26)$$

According to (26), a plot of H^{-1} versus V^E should be linear. However, when H^{-1} is plotted against V^E , a nonlinear plot was obtained in the present study. However, when $\ln H$ is plotted against G^E , a single straight line with a nonzero intercept was obtained in Figure 9. This type of result is not unexpected, because the expression for G^E takes into account both viscosity and volume. Also, in all these systems, positive η^E and negative V^E and vice versa have been observed for most of the concentration range. This behaviour was also observed by Palepu et al. [29] in binary mixtures o-chlorophenol with substituted anilines.

From the literature, no clear cut theoretical basis has been proposed for the prediction of nonideal behaviour of the binary mixtures in terms of their σ^E values. However, recently, Papaioannou and Panayiotou [30] have correlated the sign of σ^E values with η^E values and the deviations from Raoult's law. Their observation reveals the following.

- (1) Corresponding to the positive enthalpies of mixing (H^E), positive volume of mixing (V^E) and positive deviations from Raoult's law, σ^E values, have been observed to be negative.
- (2) Corresponding to the negative enthalpies of mixing (H^E), negative volume of mixing (V^E) and negative deviations from Raoult's law, σ^E values have, been observed to be positive. As shown in Figures 7 and 8, the excess surface tension (σ^E) values are negative for CA + BEN system and are positive for CA + ACT system. The positive values of excess surface tension (σ^E) increase with the rise in temperature in all systems. The negative value of σ^E in CA + BEN system is due to the predominance of the following factors: homopolymer complex formation and the tendency of the component with lower surface tension to be adsorbed at the interface. But in CA + ACT system complex formed are block copolymer $[\text{CA}]_n[\text{ACT}]_m$ and also dipole-dipole interactions between carboxylic functional group of CA and carbonyl group of ACT in the bulk phase rather than in the interface.

The interaction parameters of various models used can change with temperature but not with composition, but the interaction parameter ϕ_{12} in Rice and Teja and Rice models, based on the theory of corresponding states, has been shown to be independent of temperature and composition [19, 20]. It is observed that the models of McAllister, Auslander, and Teja and Rice fit the experimental viscosity data very well as compared to the Heric and Krishnan and Laddha models. Surface tension data is well predicted by the empirical two-parameter model [21] as well as by Rice and Teja model. The Zihao & Jufu model, based on the work of Hildebrand & Scott [31], also predicts satisfactory results for the systems studied.

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