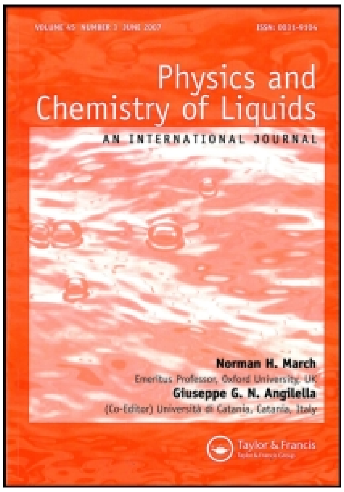

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Excess Volume and Viscosity of Propionic Acid in Methanol, Ethanol, 1-propanol and 1-butanol

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Excess Volume and Viscosity of Propionic Acid in Methanol, Ethanol, 1-propanol and 1-butanol

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Densities and viscosities of propionic acid in methanol, ethanol, 1-propanol and 1-butanol have been measured at 308.15 K. From experimental data the excess volume (V^E), excess viscosity (η^E) and the excess molar Gibbs free energy for the activation of flow (G^{*E}) have been computed and presented as functions of composition. The parameter 'd' of the Grunberg and Nissan expression has been calculated. The results indicate A–B type interaction which decreases in strength with an increase in the chain length of alcohols.

Key Words: Chain length, alcohols, Gibbs energy.

INTRODUCTION

In continuation of our work on physico-chemical properties of propionic acid + anilines[1] and + cyclohexanes[2], we report here excess viscosity and excess molar volume and other properties of propionic acid + methanol, + ethanol, + 1-propanol and + 1-butanol.

EXPERIMENTAL

Densities were measured using 18 mL bicapillary pycnometer having a capillary diameter of 0.85 mm. The pycnometer was calibrated using double distilled water (density 994.06 Kg m^{-3} at 308.15 K). All weighings were done on a Mettler balance ($\pm$ 0.05 mg). The necessary

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buoyancy correction was applied. The density values were reproducible within ± 0.2 Kg m^{-3}. A thermostatically controlled water bath, capable of maintaining the temperature constant to ± 0.02 K was used in the studies.

Viscosities of the pure liquids and the liquid mixtures were determined with a modified Ostwald viscometer. The time of efflux of a constant volume of liquid through the capillary was measured with the help of a pre-calibrated ROCAR stop-watch capable of recording ± 0.1 sec. This viscometer was always kept in a vertical position in a water thermostat at 308.15 ± 0.02 K. The efflux time for water at 308.15 K was about 302 sec. The flow time was maintained at deliberately higher value to minimize the kinetic energy correction.

The viscosity was calculated from the average efflux time 't' and density ρ according to

$$\frac{\eta}{\rho} = at - b/t \qquad (1)$$

where a and b are the characteristic constants of the viscometer. These were determined by taking water and benzene as the calibrating liquids. The kinetic energy corrections were calculated from these values and they were found negligible. The viscosity measurements were accurate to $\pm 0.5 \times 10^{-4}$ Kg $m^{-1} s^{-1}$.

Propionic acid (from Fluka, puriss, grade, purity $\gg$ 99 mole percent $C_2H_5CO_2H$) was dried over anhydrous sodium sulphate and fractionally distilled. The fraction distilling at 412.15 – 415.15 K was collected and refractionated over potassium permanganate. The middle fraction distilling at 413.85 K and 760 mm was collected. Methanol, ethanol, 1-propanol and 1-butanol supplied by BDH (AnalaR reagent grade) were further purified according to the recommended methods[3,4] and used in the studies. Purity of the solvents was confirmed by comparing the measured densities with those reported in literature (Table 1).

Table 1 Densities of liquids at 308.15 K

Liquid	ρ(Kg m^{-3})	
	Measured	Literature (3, 4)
Propionic acid	978.2	978.0
Methanol	777.4	777.0
Ethanol	776.6	776.8
1-Propanol	792.1	791.6
1-Butanol	798.7	798.7

Mixtures were prepared by mixing weighed amounts of the pure liquids adopting the closed system technique. Caution was taken to prevent evaporation.

RESULTS

The excess functions η^E and V^E, Grunberg & Nissan's[5] factor 'd'' and excess Gibbs free energy for activation of flow G^{*E} were calculated respectively from Eqs [2], [3], [4] and [5]

$$\eta^E = \eta - [X\eta_1 + (1 - X)\eta_2] \tag{2}$$

$$V^E = V - [XV_1 + (1 - X)V_2] \tag{3}$$

$$\ln \eta = X \ln \eta_1 + (1 - X) \ln \eta_2 + X(1 - X)d' \tag{4}$$

$$G^{*E} = RT[\ln \eta V - X \ln \eta_1 V_1 - (1 - X) \ln \eta_2 V_2] \tag{5}$$

The molar volume V of a mixture is calculated using Eq. (6)

$$V = \bar{M}/\rho \tag{6}$$

where $\bar{M} = XM_1 + (1 - X)M_2$, X is mole fraction of component 1, M_1 & M_2 are molecular weights of components 1 & 2 respectively. The results are presented in Table 2.

Each set of results was fitted to the following empirical Eq. (7)

$$A^E = X(1 - X)[A_0 + A_1\{X(1 - X)\} + A_2\{X(1 - X)\}^2] \tag{7}$$

where A^E represents the excess properties under consideration A_0, A_1 and A_2 are constants. The method of least squares is used to determine the values of the constants. The values of these constants along with the standard deviation (σ) defined by

$$\sigma = [\textstyle\sum(A^E_{\text{obsd}} - A^E_{\text{cald}})^2/n - 3]^{1/2} \tag{8}$$

are given in Table 3, where n is the total number of measurements. Figures 1, 2, 3 show the plots of v^E, η^E and G^{*E} versus mole fraction of propionic acid.

DISCUSSION

It is seen from the results in Table 2 that there is contraction in the molar volume for the systems studied. The maximum contraction occurs at ≈ 0.6 mole fraction of propionic acid for each of the systems (Figure 1). This suggests complex formation between propionic acid

Table 2 Experimental values of density (ρ), viscosity (η) and the calculated values of excess viscosity (η^E), excess molar volume (V^E), excess molar free energy of activation of flow (G^{*E}) and Grunberg & Nissan parameter (d') for the systems of propionic acid + alcohols at 308.15 K.

X_1^a	ρ (Kg m^{-3})	$\eta \times 10^4$ (Kg m^{-1} S^{-1})	$\eta^E \times 10^4$ (Kg m^{-1} S^{-1})	V^E (cm^3 mol^{-1})	G^{*E} (cal mol^{-1})	d'
			Propionic acid + methanol			
0.0000	777.4	4.950	0.000	0.0000	0.00	0.000
0.0467	797.0	5.336	0.196	−0.1629	32.55	1.057
0.0975	817.1	5.843	0.496	−0.3523	72.60	1.220
0.1570	837.5	6.175	0.586	−0.4946	88.34	0.954
0.2234	859.3	6.789	0.930	−0.7084	124.27	1.049
0.3021	880.7	7.413	1.235	−0.8397	151.92	1.057
0.3923	902.3	8.094	1.548	−1.0412	173.99	1.076
0.5024	927.2	9.055	2.062	−1.2486	200.37	1.211
0.6344	950.6	9.763	2.382	−1.3458	194.29	1.288
0.7111	953.1	10.210	2.396	−1.3068	174.00	1.449
0.7964	963.9	9.955	2.218	−1.1502	145.13	1.364
0.8919	950.9	9.369	1.479	−0.8540	76.00	1.070
1.0000	978.2	8.894	0.000	0.0000	0.00	0.000
			Propionic acid + ethanol			
0.0000	776.6	9.656	0.000	0.0000	0.00	0.000
0.0674	815.2	10.349	0.736	−0.2142	30.14	0.795
0.1373	831.8	10.623	1.056	−0.3072	50.81	0.698
0.2156	849.6	10.951	1.433	−0.4032	74.35	0.712
0.2983	868.0	11.250	1.784	−0.5269	93.49	0.741
0.3898	886.3	11.510	2.103	−0.6001	114.98	0.785
0.4885	905.7	11.675	2.331	−0.6668	128.84	0.841
0.5987	925.0	11.603	2.329	−0.6714	131.15	0.892
0.7173	943.1	11.192	1.994	−0.5668	115.95	0.934
0.7834	952.4	10.815	1.659	−0.4784	98.77	0.951
0.8532	961.6	10.428	1.316	−0.3608	80.41	1.050
0.9225	969.5	9.581	0.514	−0.1773	32.84	0.746
1.0000	978.2	8.894	0.000	0.0000	0.00	0.000
			Propionic acid + 1-propanol			
0.0000	792.1	14.091	0.000	0.0000	0.00	0.000
0.0416	800.2	14.200	0.121	−0.0888	8.08	0.660
0.0840	839.4	14.434	0.242	−0.1702	14.18	0.800
0.1244	816.0	14.385	0.425	−0.2189	22.02	0.700
0.1683	826.6	13.684	0.478	−0.2937	28.07	0.327
0.2579	844.0	13.514	0.732	−0.3586	42.00	0.383
0.3504	862.2	13.282	0.968	−0.4310	56.05	0.427
0.4481	880.9	12.891	1.073	−0.4692	64.18	0.449
0.5489	899.6	12.420	1.114	−0.4689	69.09	0.480
0.6538	918.9	11.779	1.005	−0.4260	65.51	0.498
0.7644	938.9	10.959	0.843	−0.3633	52.06	0.499
0.8223	948.5	10.546	0.627	−0.3005	45.16	0.529
0.8798	958.5	10.062	0.434	−0.2052	32.56	0.528
0.9384	968.2	9.669	0.238	−0.1060	12.06	0.551
1.0000	978.2	8.894	0.000	0.0000	0.00	0.000

Table 2 (*continued*).

X_1^a	ρ (Kg m^{-3})	$\eta \times 10^4$ (Kg m^{-1} S^{-1})	$\eta^E \times 10^4$ (Kg m^{-1} S^{-1})	V^E (cm^3 mol^{-1})	G^{*E} (cal mol^{-1})	d'
			Propionic acid + methanol			
0.0000	798.7	18.336	0.000	0.0000	0.00	0.000
0.0503	807.1	18.342	0.621	− 0.0832	10.16	1.734
0.1016	816.0	17.915	0.143	− 0.1403	18.01	0.432
0.1477	823.4	17.358	0.163	− 0.2006	26.08	0.397
0.1995	829.9	16.954	0.262	− 0.2509	34.04	0.396
0.3010	850.2	15.562	0.342	− 0.3308	44.06	0.236
0.4000	867.7	14.825	0.406	− 0.4012	52.09	0.297
0.5007	885.4	14.019	0.418	− 0.4213	53.18	0.347
0.5993	903.4	13.124	0.458	− 0.4305	55.46	0.379
0.7006	921.9	12.221	0.413	− 0.3786	55.79	0.436
0.7995	940.7	11.203	0.317	− 0.3009	45.25	0.466
0.9007	959.6	10.195	0.183	− 0.1829	31.67	0.152
1.0000	978.2	8.894	0.000	0.0000	0.00	0.000

[a] mole fraction of propionic acid

Table 3 Parameters of Eq. (7) and standard deviation (σ) of experimental Avalues at 308.15 K[a].

System	Function	A_0	A_1	A_2	σ
PA + MeOH	η^E	1.662	5.623	5.230	0.539
	V^E	−4.876	−3.007	−2.125	0.218
	G^{*E}	781.2	82.01	24.38	58.31
PA + EtOH	η^E	0.917	−0.035	0.053	0.129
	V^E	−2.591	0.043	− 0.038	0.291
	G^{*E}	520.7	78.41	−36.01	55.17
PA + 1-PrOH	η^E	0.445	0.052	−0.106	0.019
	V^E	−1.869	0.037	−0.355	0.071
	G^{*E}	273.9	48.17	−64.16	26.33
PA + 1-BuOH	η^E	0.061	−0.128	0.587	0.308
	V^E	−1.674	− 0.259	−0.240	0.059
	G^{*E}	219.7	80.64	85.04	11.55

[a] Units η^E, Kg m^{-1} s^{-1}; V^E, cm^3 mol^{-1}; G^{*E}, cal mol^{-1}:

and the alcohol. Further the molar volume contraction at the maximum decreases from 1.34 for propionic acid-methyl alcohol system to 0.34 for propionic acid-*n*-butyl alcohol system. This trend is traced to the different degrees of association of pure components as well as to the strength of the complex formed between the acid and the alcohol.

Carboxylic acids and alcohols are known to exist as associated liquids. The association error[6] or the association factor (S)[7] of asso-

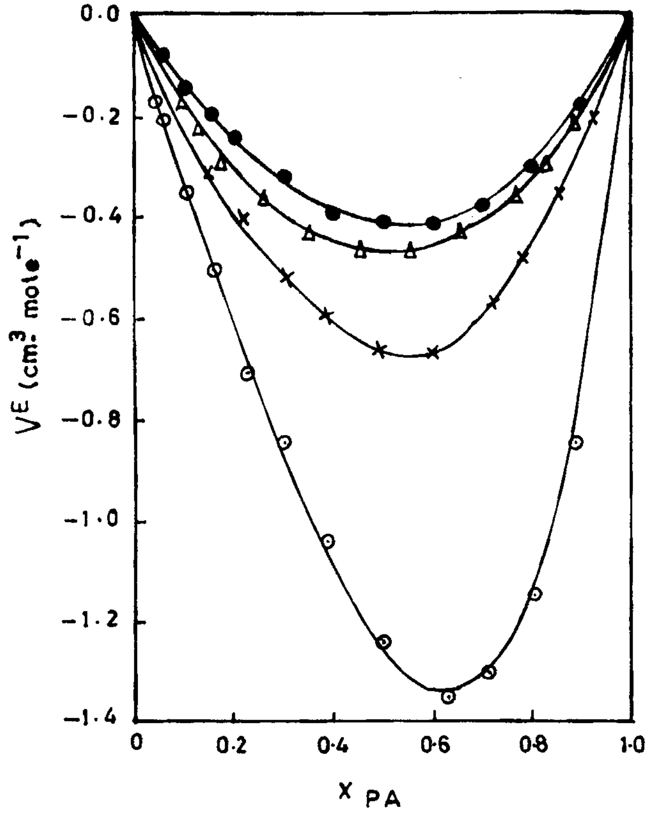


Figure 1 Excess volume at 308.15 K for mixture of propionic acid + methanol (○); + ethanol (×); 1-propanol (△); + 1-butanol (●).

ciated liquids is calculated on the assumption that (a) the dipolemoment in the vapour state is the dipolemoment of the molecule without any interaction with the surrounding molecules and (b) the dipole moment in the liquid state is the dipole moment of the molecule in interaction with the surrounding molecules. The departure of the association factor from unity is taken as a measure of the degree of association in the liquid state. The association factor[6] for propionic acid and alcohols is estimated to be less than and greater than unity respectively. It is also reported[6] that S value decreases in sequence from methyl alcohol ($S = 2.503$) to *n*-butyl alcohol ($S = 2.060$). This indicates that the association decreases from methyl alcohol to *n*-butyl alcohol.

The complex formation between propionic acid and alcohols may involve two steps, namely the dissociation[8] of the associated units to

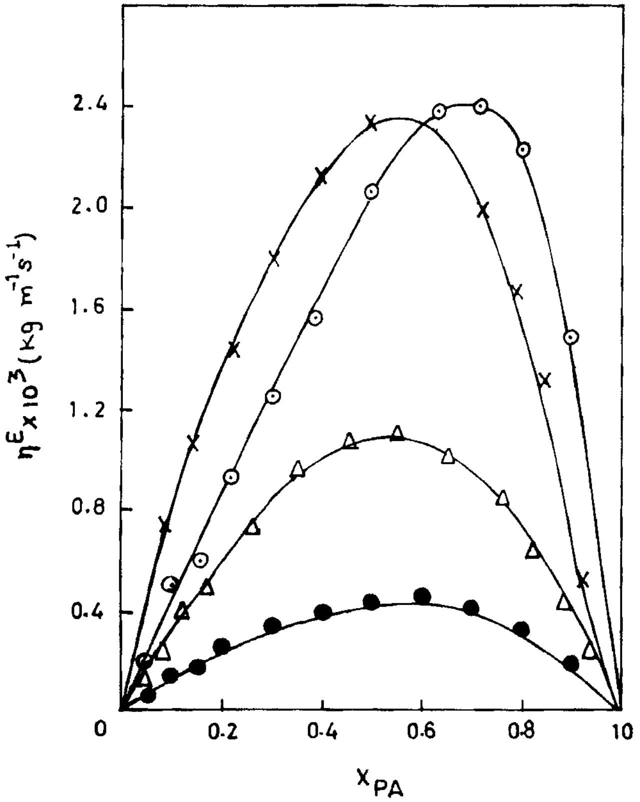


Figure 2 Excess viscosities at 308.15 K for mixtures of propionic acid + methanol (○); + ethanol (×); + 1-propanol (△); + 1-butanol (●).

give monomer molecules (resulting in the increase of OH and COOH groups) and the formation of a complex molecule between 1 mole of propionic acid and 1 mole of alcohol. Obviously these two steps are more pronounced in methyl alcohol than in *n*-butyl alcohol. The complex formation depends also on the solubility of alcohols in propionic acid. The solubility decreases from methyl alcohol to *n*-butyl alcohol and hence the complex formation is expected to decrease from methyol alcohol to *n*-butyl alcohol.

Figures 2 and 3 show positive excess viscosities and positive excess molar free energy of activation of flow with well marked maxima for all the systems. This behaviour is an evidence for the formation of complex. The symmetric curves of η^E and G^{*E} vs mole fraction for PA + MeOH indicates that the energy necessary to break the hydrogen bonds in mixing process for the pure liquids is similar for both components.

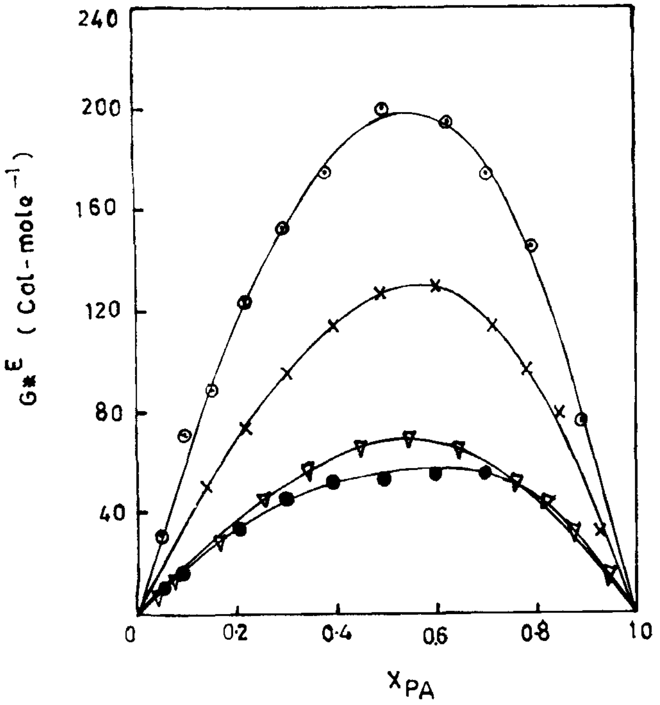


Figure 3 Excess free changes of activation of flow at 308.15 K for mixtures of propionic acid + methanol (○); + ethanol (×); + 1-propanol (∇); 1-butanol (●).

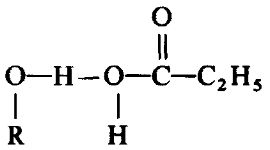
η^E has been found to be positive for all the four systems. But it becomes increasingly positive as we move from 1-butanol to methanol. This suggests progressively stronger interaction of propionic acid with methanol, ethanol, 1-propanol and 1-butanol. A similar conclusion can be drawn from the values of G^{*E} which are positive and in the following order

$$\text{MeOH} > \text{EtOH} > \text{PrOH} > \text{BuOH}$$

According to Fort and Moore[9] and Ramamoorthy[10], systems exhibit strong interactions if the parameter 'd^1' is positive and weak interactions if it is negative. On this basis also we can say that the interaction is in the following order

$$\text{PA} + \text{MeOH} > \text{PA} + \text{EtOH} > \text{PA} + \text{PrOH} > \text{BuOH}$$

The results suggest A-B type of interaction forming intramolecular hydrogen bond



$$\underset{\displaystyle R}{\underset{|}{O}}-H-\underset{\displaystyle H}{\underset{|}{O}}-\overset{\displaystyle O}{\overset{\|}{C}}-C_2H_5$$

The strength of bonding is expected to decrease with the increase in chain length of the alcohol. The results in the present study corroborate this fact.

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