

## Excess Molar Volumes and Viscosities of Water +2-Propanol at 298.15, 303.15 and 308.15 K

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**Summary:** Excess molar volumes and viscosities were calculated for water +2-Propanol mixtures in all mole fraction ranges at three different temperatures, i.e. 298.15, 303.15 and 308.15K. Values of excess molar volume have been found negative for all the temperatures studied and passed through a minima at almost 0.3 mole fraction of 2-propanol. Viscosities,  $\eta$ , are presented as a polynomial in mole fraction  $x_1$  of low molecular weight component of binary mixture:  $\eta = A + BX_1 + CX_1^2 + DX_1^3 + EX_1^4$ .

### Introduction

Alcohol-water systems are studied from many points of view and the literature on this system is available which report various parameters like densities [1-3], viscosities [4,5], partial molar volume [6], excess thermodynamic functions [7,8], etc. This paper reports the excess molar volume and viscosities of water +2-propanol mixtures at three different temperatures. The viscosity data were fitted to the empirical relationships of McAllister [9], Heric [10] and Auslander [11] and also to three different polynomials [12] with a goodness of fit approximating experimental error. These equations are given below:

#### McAllister's formula [9]

$$\ln \eta = x_1^3 \ln \eta_1 + 3 x_1^2 x_2 \ln \eta_{12} + 3 x_1 x_2^2 \ln \eta_{21} + x_2^3 \ln \eta_2 + D'$$

where  $D' = -\ln(x_1 + x_2 M_2/M_1) + 3x_1^2 x_2 \ln(2/3 + M_2/3M_1)$

$$+ 3x_1 x_2^2 \ln(1/3 + 2M_2/3M_1) + x_2^3 \ln(M_2/M_1)$$

The equation contains two adjustable parameters

$\ln \eta_{12}$  and  $\ln \eta_{21}$ .

#### Herrics formula [10].

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 \ln M_1 + x_2 \ln M_2 - \ln(x_1 M_1 + x_2 M_2) + \Delta_{12}$$

Where  $\Delta_{12} = \alpha_{12} + X_{12} X_{21}$  is a function representing molecular interaction and  $X = X$  is the interaction parameter. Heric expressed.

$\alpha_{12} = \alpha^{21}$  as a linear function of composition

$$\alpha_{12} = \beta_{12} + \beta_{21} (x + x_2)$$

The coefficients  $\beta_{12}$  and  $\beta_{21}$  may be determined from a least-squares method.

#### Auslander' formula [11]

$X_1 (X_1 + B_{12} X_2) (\eta - \eta_1) + A_{21} X_2 (B_{21} X_1 + X_2) (\eta - \eta_2) = 0$  Here  $A_{21}, B_{12}$  and  $B_{21}$  are the parameters representing binary interactions.

#### Polynomial functions [12]

##### Polynomial I

$$\eta = A + B X_1 + C X_1^2 + D X_1^3 + E X_1^4$$

Where A,B,C,D and E are adjustable parameters

##### Polynomial II

$$\eta = \eta_1 x_1 + \eta_2 x_2 + A X_1 + B X_2 + X_1 X_2 [A + B (X_1 - X_2) + C (X_1 - X_2)^2]$$

##### Polynomial III

$$\eta = \eta_1 X_1 + \eta_2 X_2 + X_1 X_2 [A + B(X_1 - X_2) + C (X_1 - X_2)^2]$$

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Here again, A, B and C are adjustable parameters and could be determined by a weighted least square method.

### Results and Discussion

Excess molar volumes were calculated from measured densities of pure components and the binary mixtures using relationship [13].

$$V_M^E = [(1-x) M_1 + x M_2] / \rho - (1-x) M_1 / \rho_1 - x M_2 / \rho_2 \quad (1)$$

Where  $M_1$  and  $M_2$  denote the molar masses and  $\rho_1$  and  $\rho_2$  the densities of pure liquids,  $\rho$  the density of the mixture and  $x$  is the mole fraction. The values of  $V_M^E$  are reported in Table-1 and also shown in Figure 1. The experimental values of  $V_M^E$  were fitted to the equation [14].

$$V_M^E / (\text{cm}^3 \cdot \text{mol}^{-1}) = x(1-x) [A_0 + A_1$$

$$(2x-1) + A_2(2x-1)^2 + A_3(2x-1)^3] \quad (2)$$

The parameters  $A_0$ ,  $A_1$ ,  $A_2$  and  $A_3$  are adjustable parameters and were evaluated by the method of least squares with all points weighted equally. The standard deviations were calculated by using the equation:

$$S(V_M^E) = [(V_{\text{expt}}^E - V_{\text{calcd}}^E)^2 / (n-p)]^{1/2} \quad (3)$$

The values of the parameters, in along with the standard deviations  $S(V_M^E)$  are given Table-2. Both alcohols and water are known to be associated through hydrogen bonding [8,15,16]. However the dipole moment values of water is reportedly higher than alcohols [17]. Mixing of water and 2-propanol in all mole fractions causes the excess molar volume to decrease below zero. These typical values are shown in Table-1 and in Figure 1. The excess molar volume is negative for all the three different temperatures selected for this study. In the higher and lower mole fraction region, the curves

Table-1: Excess molar volumes and densities of mixtures of water and 2-propanol at different temperatures.

X	Density	Density	Density	$V_M^E$	$V_M^E$	$V_M^E$
	at	at	at	at	at	at
	298.15	303.15	308.15	298.15	303.15	308.15
0.0320	0.9809	0.9788	0.9771	-0.1953	-0.1931	-0.2022
0.0698	0.9676	0.9642	0.9616	-0.4862	-0.4652	-0.4649
0.1139	0.9484	0.9453	0.9420	-0.6657	-0.6600	-0.6513
0.1376	0.9385	0.9352	0.9316	-0.7333	-0.7264	-0.7133
0.1665	0.9270	0.9235	0.9198	-0.7933	-0.7853	-0.7729
0.3051	0.8848	0.8815	0.8781	-1.0044	-1.0240	-1.0397
0.5319	0.8359	0.8316	0.8273	0.7861	-0.7778	-0.7659
0.7156	0.8105	0.8060	0.8017	-0.4565	-0.4408	-0.4336
0.8517	0.7979	0.7937	0.7894	-0.2855	-0.2988	-0.2958

Units of Density =  $\text{g} \cdot \text{cm}^{-3}$   
Units of  $V_M^E$  =  $\text{cm}^3 \cdot \text{mol}^{-1}$ .

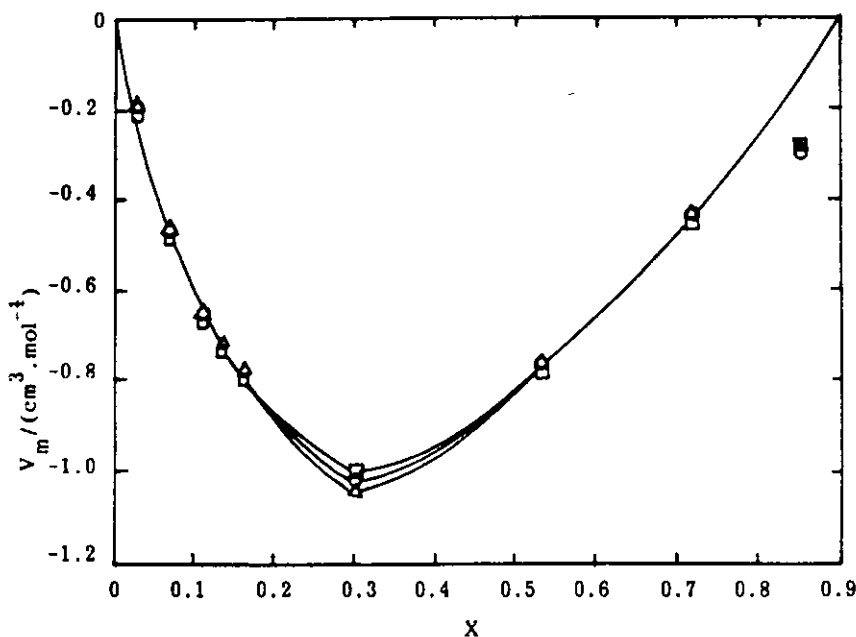


Fig. 1: Excess molar volume  $V_m^E$  of water +2-propanol vs mole fraction 2-propanol.  $\Delta$ 298.15K,  $\circ$  303.15K,  $\square$  308.15K.

Table-2: Parameters of equation 2 and the standard deviation  $S(V_M^E)$ 

Temp. K	$A_0$	$A_1$	$A_2$	$A_3$	$S(V_M^E)$ $\text{cm}^3 \cdot \text{mol}^{-1}$
298.15	-3.3012	3.1768	-1.6846	-8.380	0.0413
303.15	-3.2880	3.4154	-1.7981	-1.4384	0.0290
308.15	-3.3221	3.5276	-1.9461	-1.3528	0.0358

of excess volume vs mole fraction shows an overlap, whereas, in the remaining region (0.2-0.6 mole fraction) the curves fall apart showing a minima of  $V_M^E$  for mixtures almost at 0.3 mole fraction of 2-propanol. Value of  $V_M^E$  is minimum at 308.15K and show a gradual increase as the temperature is raised. This seems to be in agreement with the nature of the solvents selected for this purpose and can be attributed entirely to the physical interaction between water and 2-propanol molecules. It is expected that preferred hydrogen bonding between the two solvents give rise to this effect. Negative values of  $V_E^M$  for the liquid systems are explained in terms of different size of the molecules or the dipole-dipole interactions between them. Values of  $V_M^E$  show that the association between unlike molecules predominates over dissociation.

Viscosities of binary mixtures of water + 2-propanol were measured at 298.15, 303.15 and 308.15K. The experimental values obtained were fitted to McAllister, Auslander, and Heric's equations and also to three polynomials. The average values for the root mean square (rms) for all mixtures investigated are given in Table-3. The rms values of McAllister and Heric equations are for the natural logarithm of the rms, whereas that of Auslander's is in terms of viscosities and thus cannot be compared directly. It should be noted that all equations tested except polynomial I included fixed end values such that the experimental values of the pure components do not participate in the error determination. The viscosities of binary mixtures at each temperature are reported in terms of the parameters of polynomial I in Table 4. It should be noted that parameter A is the best fit absolute viscosity for the high molecular weight component of the binary mixture whereas the sum of the other four parameters is, the best fit value of the absolute viscosity of the low molecular weight component. This polynomial allows the calculation of

Table-3: RMS values for water +2-propanol mixtures at different temperatures.

Temp. K	McAllister <sup>a</sup>	Auslander	Heric <sup>a</sup>	Polynomial		
				I	II	III
298.15	0.3893	0.8023	0.1338	0.1382	0.6879	0.4024
303.15	0.2984	0.6023	0.1132	0.0821	0.5766	0.2089
308.15	0.2438	0.5788	0.1023	0.0744	0.5429	0.2778

<sup>a</sup>Rms in logarithm form

Table-4: Values of various parameters for the equation  $\eta = A + Bx_1^2 + Cx_1^2 + Dx^3 + Ex_1^4$  fitted to viscosity data of water + 2-propanol at various temperatures.

Temp. K	A	B	C	D	E	rms error
298.15	2.1189	6.1905	-29.5638	56.2818	-34.3096	0.1382
303.15	1.7271	5.9032	-27.1148	48.8611	-28.6776	0.0821
308.15	1.6355	4.8476	-19.3786	33.3226	-19.7716	0.0744

viscosities of any mole fraction of the mixture within the rms error reported.

### Experimental

All chemicals used in this work were obtained from Merck and were further purified as suggested in the literature [18]. Water was triply distilled according to standard procedure and the purity was checked by measuring the densities and refractive index values and comparing them with the reported values [18-19]. Excess molar volumes at various temperatures were determined from density data. Mixtures were prepared by mass using a Metler AE 240 balance with a precision of  $\pm 0.1$  mg. Densities were measured to a precision of  $\pm 0.0001$  g/cm<sup>3</sup> on DMA 48 (AP-PAAR Austria) density meter. This technique required two density standards, we used freshly distilled water and air. Kinematic viscometer was used to measure the viscosity of water  $\pm$ 2-propanol mixtures at three temperatures. Triply distilled water was used to calibrate the viscometer. Efflux times were noted by a digital counter of 0.01 s resolution. Computation of the kinematic viscosity is done by using the relation.

$$\alpha = Kt$$

Where  $\alpha$  = Kinematic viscosity of a sample in cSt, K = capillary constant of the viscometer in cSt/s, and t = time of flow in second. The kinematic viscosities were adjusted for kinetic energy by using the Hagenbach correction [20].

Absolute viscosity values were then determined by using the relation.

$$\eta = \alpha\rho.$$

Where  $\eta$  = absolute viscosity of a sample in cP and  $\rho$  = density of a sample in g/ml.

Dedication: This paper is dedicated to the memories of late Dr. M.S.K. Niazi.

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