Delta J. Sci. 16 (1) 1992 , 91-110

ASPECTS OF PHYSICO-CHEMICAL PROPERTIES OF n-PROPYL ALCOHOL-WATER MIXTURES AT DIFFERENT TEMPERATURES

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Received: 29-1-1992

ABSTRACT

Dielectric constants and the loss in their values, for n-propyl alcohol-water mixtures have been measured at different temperatures and at constant frequency (2 MH_z). The variation of the dielectric constant properties with both temperature and alcohol content was discussed.

Absolute density for the same mixtures has been measured at different temperatures. Solute-solvent interactions studied and the dielectric constant and density measurements indicated the existence of the molecular complex (1 n-PrOH: $2H_2O$) due to the hydrogen bond formation.

INTRODUCTION

For studying the properties of organic and mixed organic solvents a great need of knowledge concerning physico-chemical properties is required, such as, dielectric constant properties, density, solvation, viscosity, molar volume and acidity function. Attention is largely withdrawn to monohydric alcohol-water mixtures, for these are of greatest interest from the structural view point [1].

The relatively simple alcohol-water mixtures may surve as helpful models for better understanding of more complex systems. Alcohol-water mixtures have been extensively used to study the influence of the dielectric constant of the solvent on equilibria and rates of reactions in which charge centers are produced or neutralized.

Solute-solvent interaction in alcohol-water systems is of great interest [2-4]. The main assumption involved is that liquid water exists in the form of aggregates, in which water molecules are connected into a network-like structure through hydrogen bonds [5]. The aggregates can take many shapes depending on the number of sharing molecules [1,6,7]. Contraction in volume is observed in many systems [1, 3, 8-10], on mixing alcohol with water, due to the occupation of free volume or cavities in the open solvent structure by the other component. This phenomenon is called excess volume (ΔV) which gives an indication of the strength of solute-solvent interaction, and can be calculated from density measurements using different equations [3,11]. The deviation between the observed and calculated dielectric constant ($\Delta \epsilon'$) also was taken as a measure of this interaction [12].

In this study, dielectric constants and the loss in their values (at 2 MH_z) and absolute densities were measured for various compositions of n-PrOH-H_2O mixtures at different

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temperatures. The results were used to apply Akerlof linear relationship [13], and in calculating the molar polarization (P_{12}), volume contraction (δ) and excess volume (ΔV), to give a measure of the possibility of solute-solvent interaction in this polar-polar system. The results were compared with those obtained using dielectric constant deviation ($\Delta\epsilon'$).

EXPERIMENTAL

1- Materials

Conductivity water was prepared from the doubly distilled H_2O acording to the method of Gayer [14].

n-Propyl alcohol used was of AnalaR grade, and was further purified according to the recommended method [13]. The purity of the substance was checked by measuring the density, d, and the dielectric constant, ϵ'.

2- Measurements

The dielectric constant, ϵ', and the loss in its value, ϵ'', were measured [15], by a Multidekameter type DK06, which has a frequency band 0.2 to 10 MH_z.

The absolute densities, d (g/ml) were measured by the usual Sprengel-Ostwald pyknometer where the method of Smyth [16] was used. The observed values were in agreement with those found in the literature [13].

RESULTS AND DISCUSSION

Dielectric constant and loss in its value for n-PrOH-H_2O mixtures were measured at constant frequency (2 MH_z) and at different temperatures. The variation of the dielectric constant (ϵ') with temperature obeys the linear relationship [13]:

$$\epsilon'_t = a\ t + b$$

where, a is the thermal variation of ϵ', i.e., $d\epsilon'/dt$, and b is a constant obtained from the least squares method. Values of the coefficients a and b are tabulated in Table 1. Hence for any solvent mixture with known ϵ' & b, the temperature coefficient of permitativity ($d\epsilon'/dt$) which is characteristic for it can be calculated.

Table (1) Values of a, b and deviation between $\epsilon'_{obs.}$ & $\epsilon'_{calc.}$ ($\Delta\epsilon'$) for n-propyl alcohol-water mixtures at different temperatures.

$X_{alc.}$	a	b	($-\Delta\epsilon'$) 20°C	30°C	40°C	50°C
0.0000	-0.366	89.12	0.00	0.00	0.00	0.00
0.0322	-0.418	82.23	5.80	6.49	6.74	6.31
0.0597	-0.345	74.53	10.39	9.86	10.70	10.34
0.1138	-0.327	65.14	15.79	16.35	15.29	14.02
0.1665	-0.300	56.52	20.67	19.36	19.42	18.26
0.2306	-0.266	48.51	24.89	24.72	23.93	23.39
0.3102	-0.200	42.06	25.70	24.19	23.59	22.21
0.4116	[illegible]	[illegible]	24.7[illegible]	22.4[illegible]	22.07	[illegible]
0.5453	-0.156	[illegible].02	21.32	19.[illegible]	18.78	17.37
0.7296	-0.160	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
1.0000	[illegible]	25.52	[illegible]	[illegible]	0.06	[illegible]

Fig. 1 shows the applicability of this relation to the system under investigation. The decrease of ϵ' with increasing temperature may be attributed to the thermal dissociation of the aggregated molecules into smaller units [17], and to the thermal activation of the dipoles in solution, which weakens the interaction between the neighbouring dipoles. Also, this decrease of ϵ' with increasing temperature may be attributed [18] to the decrease of the total amount of hydrogen bonding per unit-volume in alcohol-water systems. Eq. (1) has a great value for interpolation purposes and therefore it can be applied over a large temperature range.

Fig. 2, illustrates the variation of ϵ' with alcohol content at different temperatures which shows that ϵ' increases by increasing the water content of the medium. This is in good agreement with the behaviour of MeOH-H_2O mixtures [19,20].

On plotting the loss in dielectric constant ϵ'' vs. temperature in Fig. 3, it can be seen that ϵ'' increases with increasing temperature in contrast to the behaviour of ϵ', and there is a transition temperature between 35° and 40°C for most of the studied media. This can be attributed to the fact that viscosity decreases by increasing the temperature and accordingly the dipoles become more free to rotate in solution.

The variation of the loss in dielectric constant, ϵ'', with alcohol content (Fig. 4a), shows an increase in the value of ϵ'' on adding n-propyl alcohol to water then a decrease by increasing the concentration of the alcohol. This increase may be due to the crushing of the shield around the water molecules by the dipolar propyl alcohol which in turn increases the energy of dipoles in solution. Fig. (4b), shows the variation of the parameter "a" vs. mole fraction of n-propyl alcohol; "a" can be denoted as the energy factor in the solution [21].

The deviation between $\epsilon'_{obs.}$ and $\epsilon'_{calc.}$ ($\Delta\epsilon'$), is calculated [12] using equation 2, and the values recorded in Table 1.

$$\Delta\epsilon' = \epsilon'_{obs.} - \epsilon'_{calc.} = \epsilon'_{obs.} - (x_1 \epsilon'_1 + x_2 \epsilon'_2) \quad (2)$$

where x_1 and x_2 are the mole fractions of the two components. The plot of $\Delta\epsilon'$ vs. mole fraction of the alcohol, Fig. 6(a), shows a minimum at about $x \simeq 0.35$ indicating solute-solvent interaction and suggesting the existence of the molecular complex (1 n-PrOH: $2H_2O$).

Fig. 5 shows the variation of the calculated values of the absolute densities (d in g/ml), for n-propanol-water mixture with its composition at different temperatures.

It can readily be seen that the absolute density values decrease by increasing alcohol content, reaching the smallest, d, values at pure alcohol and the greatest ones at the pure water. This behaviour indicated that densities of n-propanol-water mixtures obey an additive rule.

To get more information about the structural variations, it is helpful to calculate both the volume contraction, (δ) and the volume change (ΔV), for n-propanol-water mixtures. Scatchard [11] equation was choosen as an example to calculate (δ) values and can be written, for any two homogenous mixtures at a given temperature as follows:

$$\delta = \frac{1}{d_{12}} - \left[\frac{W_1}{d_1^o} + \frac{W_2}{d_2^o} \right] \qquad [3]$$

where d_1^o, d_2^o and d_{12} are the absolute densities of the pure components and their mixtures, respectively, while W_1 and W_2 are their weight fractions. The following relation [3] is used to calculate volume contraction (V) of these mixtures is as follows:

$$\Delta V = \left(\frac{\Sigma XM}{d_{12}} \right) - \left[\frac{X_1 M_1}{d_1^o} + \frac{X_2 M_2}{d_2^o} \right] \qquad [4]$$

where x, M, d_1^o, d_2^o and d_{12} have the usual meaning terms.

Table 2, recorded the values of (δ) and (Δ V) for n-propanol-water mixtures, at different temperatures.

The relation between (Δ V) and the mole fraction of the alcohol $X_{alc.}$ illustrated in Fig. 6(b), the curves gave minima at $X_{alc.} \simeq 35$. This behaviour indicates inter-molecular attraction between alcohol and water through the formation of hydrogen bonds, and the possibility of existence of a molecular aggregate with the structure (1 PrOH: $2H_2O$).

Table (2) Values of volume contraction, δ, and the change in molar volume (ΔV) for n-propyl alcohol-water mixtures at different temperatures.

$X_{alc.}$	$-\delta \times 10^2$				($-\Delta$V)			
	20°C	30°C	40°C	50°C	20°C	30°C	40°C	50°C
0.0000	0.000	0.000	0.000	0.000	0.0000	0.0000	0.0000	0.0000
0.0322	0.966	0.957	0.490	0.936	0.1865	0.1847	0.1826	0.1808
0.0697	2.196	1.734	1.580	1.401	0.4597	0.3630	0.3307	0.2932
0.1138	2.215	2.015	1.826	1.636	0.5054	0.4599	0.4166	0.3735
0.1665	2.293	2.091	1.923	1.797	0.5726	0.5220	0.4799	0.4483
0.2305	2.240	2.028	1.812	1.642	0.6208	0.5621	0.5021	0.4552
0.3102	2.626	1.979	1.835	1.678	0.8159	0.6148	0.5699	0.5213
0.4116	1.896	1.755	1.610	1.484	0.6699	0.6199	0.5689	0.5241
0.5453	1.557	1.464	1.371	1.299	0.6378	0.5999	0.5613	0.5321
0.7296	0.981	0.856	0.758	0.733	0.4776	0.4171	0.3695	0.3572
1.0000	0.000	0.000	0.000	0.000	0.0000	0.0000	0.0000	0.0000

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The molar polarization for n-propanol-water mixtures was calculated from the Debye equation (22) which has the following form:

$$P_{12} = \frac{\epsilon' - 1}{\epsilon' + 2} \left(\frac{X_1M_1 + X_2M_2}{d_{12}} \right) \qquad (5)$$

where, X is the mole fraction, M the molecular weight and d is the density of the mixture. The values of P_{12} are recorded in Table 3. Fig. 7 shows the relation between P_{12} and the mole fraction X of the alcohol. A straight line is obtained similar to that obtained for some other polar-polar systems [20 , 23).

The obtained straight line does not imply that the system under investigation can be considered to represent an ideal nonreacting mixture, since calculations of (ΔV), ($\Delta\epsilon'$), (δ) and deviation in molar viscosity $\Delta\eta_{M12}$ [10] indicated solute-solvent interaction. Franks [1] gave an interpretation for the previous behaviour in alcohol-water from the competing effects on water around the organic solvent molecules.

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Table (3) Molar polarization values P_{12} of nPrOH-H_2O mixtures at different temperature.

$x_{alc.}$	20°C	30°C	40°C	50°C
0.0000	17.4018	17.4016	17.4098	17.4168
0.0322	18.9105	18.9134	18.9313	18.9589
0.0697	20.6062	20.7254	20.7761	20.8519
0.1138	22.8214	22.8720	22.9800	23.0991
0.1665	25.4155	25.5189	25.6037	25.7288
0.2306	28.4760	28.5191	28.6485	28.7578
0.3102	32.1862	32.4235	32.5409	32.7437
0.4116	37.1816	37.3652	37.4729	37.6930
0.5453	42.0993	43.6604	43.7924	44.0053
0.7296	52.5182	52.2684	52.4907	52.6698
1.0000	65.6078	65.2084	65.3669	65.4955

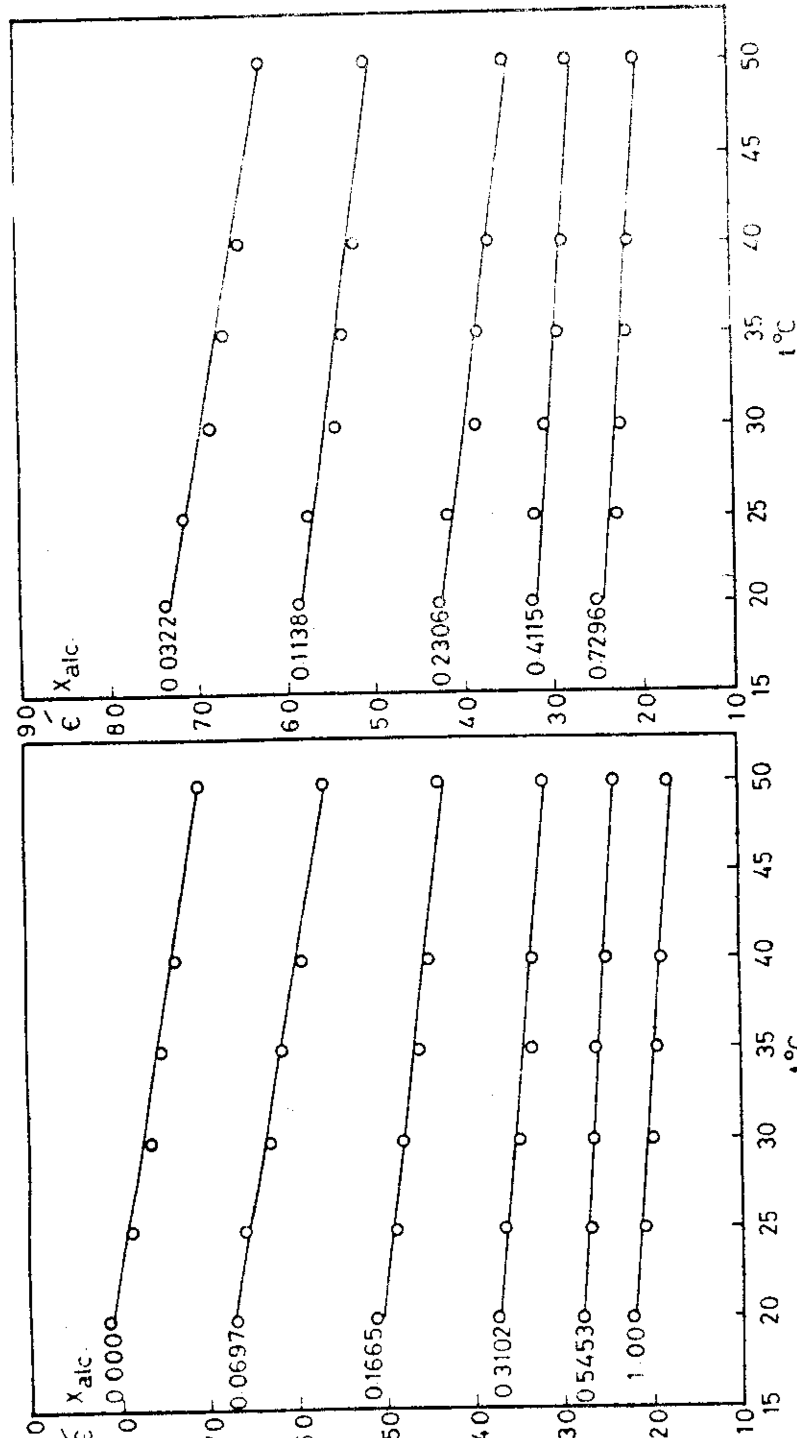

Fig.1: Variation of dielectric constant (έ) with temperature (t) for n-propyl alcohol-water mixtures at different alcohol content.

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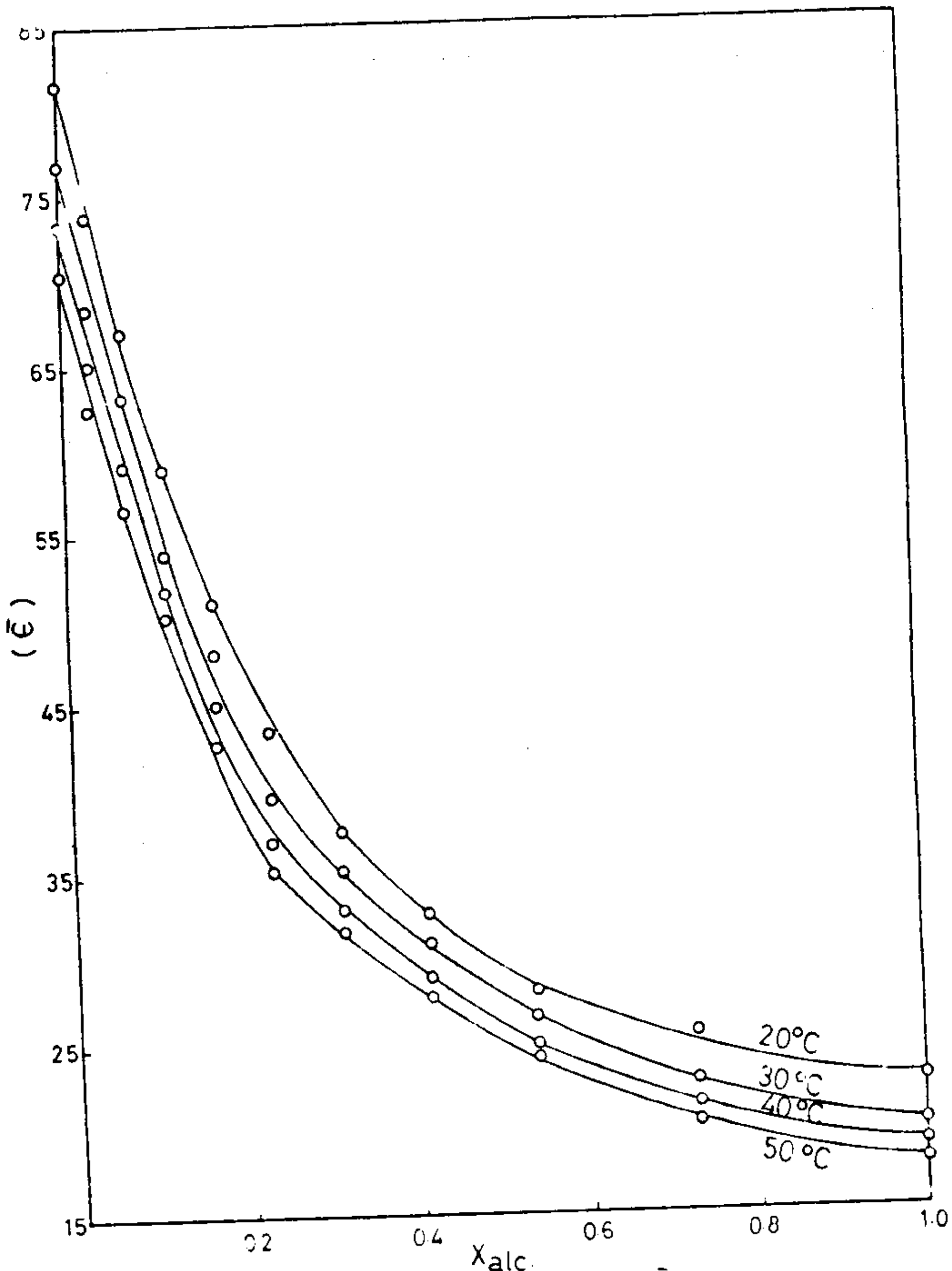

Fig. 2: Variation of dielectric constant Ē with n-propyl alcohol content at different temperatures.

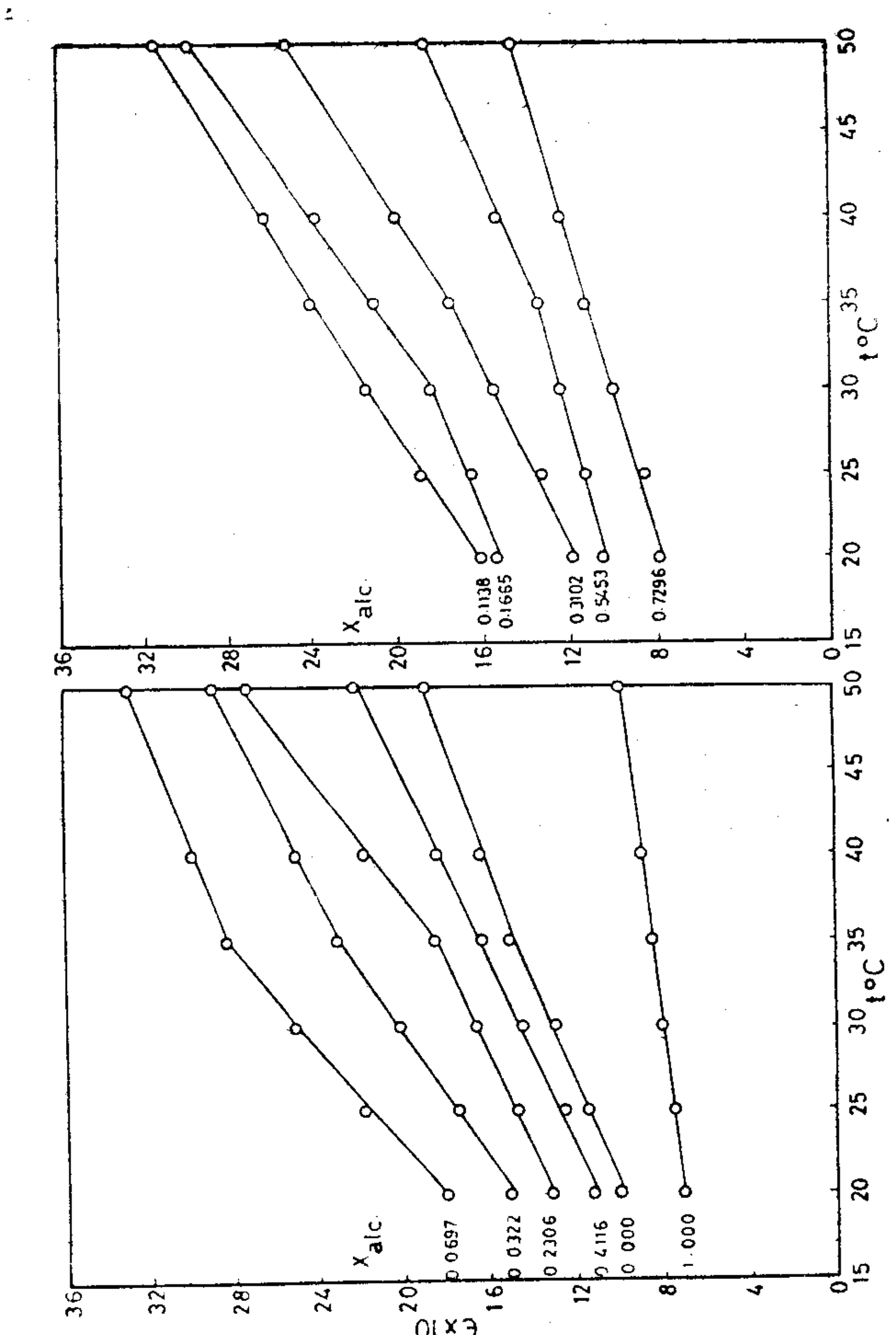

Fig. 3: Variation of the loss in dielectric constant ε″, with temperature, t, for n-propyl alcohol-water mixtures at different temperatures.

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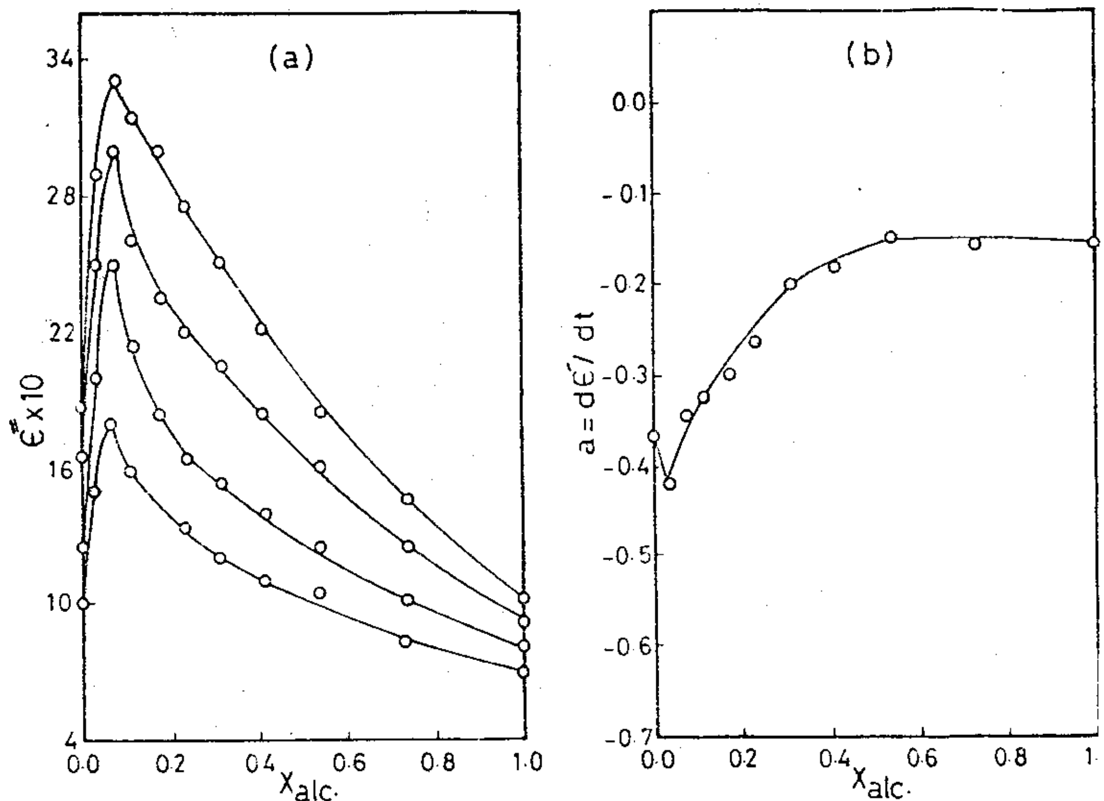

Fig. 4: Variation of (a) loss in dielectric constant (ϵ'') with alcohol content for n-propyl alcohol at different temperatures, (b) parameter, b, with alcohol content, X_{alc}.

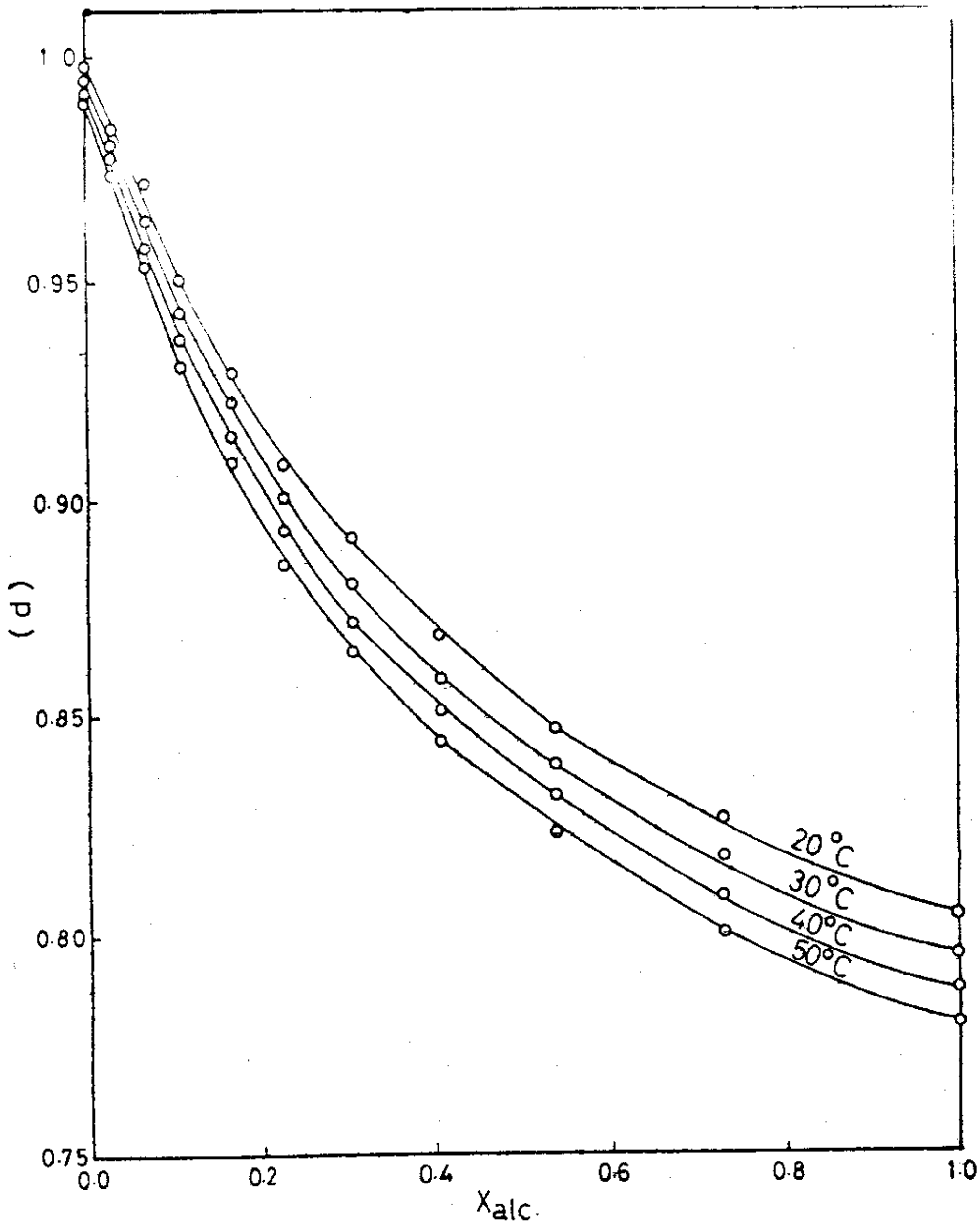

Fig. 5: Variation of absolute density, d, (gm/ml) with alcohol content for n-propyl alcohol-water mixtures at different temperatures.

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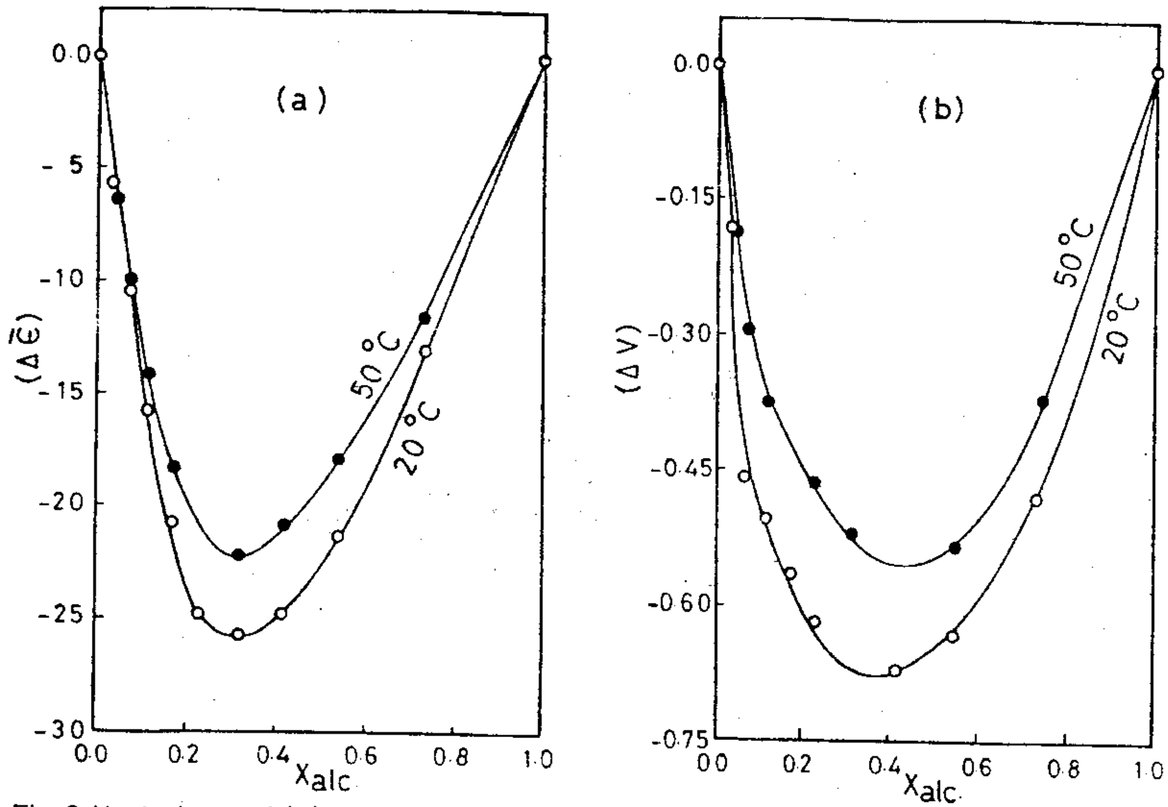

Fig.6: Variation of (a) deviation between the observed and calculated dielec constant ($\Delta\bar{\epsilon}$), (b) molar volume (ΔV) with n-propyl alcohol content at different temperatures.

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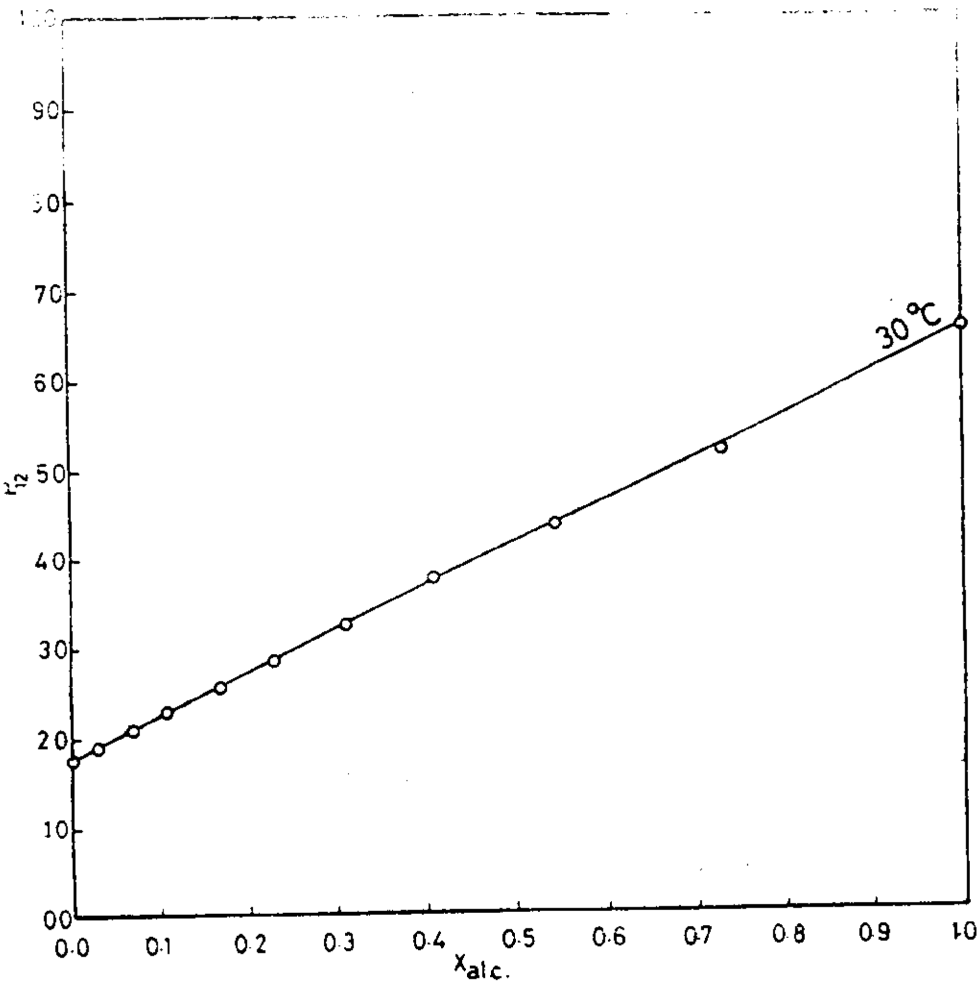

Fig.7: Variation of molar polarization P_{12} of n-propyl alcohol - water mixtures with alcohol content at 30 °C .

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أضواء على الصفات الفيزوكيميائية لمخاليط الكحول البروبيلى العادى مع الماء عند درجات حرارة مختلفة

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اجريت قياسات ثابت العزل الكهربى وثابت الفقد الكهربى لمخاليط الكحول البروبيلى العادى مع الماء عند تردد قدره ٢ ميجاهيرتز فى درجات حرارة مختلفة ولقد نوقشت العلاقة بين خواص العزل الكهربى وكل من درجة الحرارة ونسبة الكحول فى المحلول. كما تم قياس الكثافة المطلقة لهذه المخاليط ومن خلال هذه القياسات مع قياسات ثابت العزل الكهربى امكن دراسة التفاعل المترابط بين المذاب والمذيب وامكن استنتاج تواجد المتراكب الجزئى (١ كحول : ٢ ماء).