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## LIMITING ACTIVITY COEFFICIENTS OF ALIPHATIC ALCOHOLS IN PHTHALATES<sup>a</sup>

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(First received July 27th, 1988; revised manuscript received February 15th, 1989)

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### SUMMARY

Limiting activity coefficients of methanol, ethanol, 1-propanol, 1-butanol and 1-pentanol were determined in di-*n*-decyl phthalate (DNDP), diisodecyl phthalate, di-*n*-butyl phthalate and tetrachlorodibutyl phthalate at 50–100°C. In order to ascertain the surface effects at the gas–liquid interface, the limiting values were evaluated at 15, 20 and 30% column loadings for DNDP. The data, corrected for surface effects, show excellent agreement with the experimental data at a 30% column loading. The limiting activity coefficient values of these alcohols were determined at 15 and 30% column loadings for other phthalates. All the alcohols were found to show a positive deviation from Raoult's law. A decrease in the limiting value with increase in the molecular weight of the alcohols was also observed.

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### INTRODUCTION

Gas chromatography is an excellent method for obtaining equilibrium data at infinite dilution with high accuracy. These data, which indicate the solute–solvent interactions, provide a good source for evaluating UNIFAC group interaction parameters<sup>1,2</sup>, which are gaining importance in the design of fluid-phase separation equipment. In fact, the limiting activity coefficient data are very effective both in the description of binary mixtures and in scale-up to multi-component systems.

The limiting activity coefficient characterizes the behaviour of a single solute molecule completely surrounded by solvent molecules. As such, it generally indicates a maximum non-ideality and offers incisive information to the theorist, as the order–disorder effect disappears; it also offers economy of effort to the experimentalist, as the datum has wider applicability than measurement at any other

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<sup>a</sup> RRLH communication No. 2228.

concentration. Measurements in this region are difficult by conventional methods and tend to be inherently inaccurate. Conventional methods for studying solution phenomena, which depend on the measurement of vapour pressure, suffer the disadvantage that the experimental error of measurement at low concentrations is usually much greater than at higher concentrations.

Work on solution thermodynamics using gas chromatography commenced in the late 1950s<sup>3-5</sup> and useful data are still being reported. The work of Everett and Stoddard<sup>6</sup> and of Cruickshank *et al.*<sup>7</sup> was found to be more accurate. Kikic and co-workers<sup>8,9</sup> have shown that plots of the logarithm of activity coefficient at infinite dilution ( $\gamma^\infty$ ) versus inverse of temperature ( $1/T$  K) for aliphatic and aromatic solutes with phthalate ester solvents were not linear, indicating that the excess heat of mixing ( $\Delta_{He}$ ) was not constant over the temperature range investigated. Very little information is available in the literature on activity coefficients at infinite dilution of alcohols with respect to phthalates.

In this paper, a gas chromatographic method is described for determining the activity coefficients at infinite dilution of five aliphatic alcohols starting from methanol in four different phthalate stationary phases at different concentrations.

## EXPERIMENTAL

Spectroscopic-grade methanol, ethanol, 1-propanol, 1-butanol and 1-pentanol from E. Merck (Darmstadt, F.R.G.) were used.

Chromatographic grade di-*n*-decylphthalate (DNDP), diisodecyl phthalate (DIDP), di-*n*-butyl phthalate (DNBP) and tetrachlorodibutyl phthalate (TCDBP) were obtained from Analabs (North Haven, CT, U.S.A.). These phases were coated on Chromosorb W supplied by Alltech (Arlington Heights, IL, U.S.A.). The coated material was then filled in 243.8 cm  $\times$  3 mm I.D. stainless-steel columns. The columns were turned into a spiral shape and fitted in the thermostated oven of the chromatograph maintained at 100°C. Each column was conditioned for 48 h by passing 99.99% pure IOLAR Grade I nitrogen supplied by Indian Oxygen (Bombay, India).

A microprocessor-controlled Hewlett-Packard Model 5840 A gas chromatograph equipped with a thermal conductivity detector was used for determining the activity coefficients at infinite dilution of the solutes with respect to the solvents under study.

Pure hydrogen was used as the carrier gas. The flow-rate was measured by a soap-bubble flow meter to an accuracy of 0.05 ml/min. The carrier gas flow-rates were measured at ambient temperature and corrected to the experimental conditions by means of eqn. 1 (see also p. 16 of ref. 22). After attaining steady conditions in the system, 1  $\mu$ l of solute was injected and the retention time of the solute,  $t_r$ , was noted. Duplicate or triplicate runs were made for each solute. The experiment was then repeated by injecting an inert gas such as methane and its retention time,  $t_0$ , was noted.

The specific retention volume,  $V_g^0$ , was calculated according to Desty and Swanton<sup>10</sup> by means of the equation

$$V_g^0 = [(JF_m/W)(P_0 - P_{H_2O})/101325](273/T_m)(t_r - t_0) \quad (1)$$

The activity coefficient at infinite dilution ( $\gamma_2^\infty$ ) of the solute (component 2) was calculated utilizing the relationship between  $V_g^0$  and  $\gamma_2^\infty$ :

$$\ln \gamma_2^\infty = \ln(273 R/P_2^0 M_1 V_g^0) - (B_{22} - V_2^0)P_2^0/RT_{\text{exp}} \quad (2)$$

The second term in eqn. 2 takes into account the non-ideality of the gas phase<sup>11</sup>.

The second virial coefficients ( $B_{22}$ ) of the solutes at required temperatures were calculated as suggested by Hayden and O'Connell<sup>12</sup>. The necessary physical properties of all the solutes, such as vapour pressure ( $P_2^0$ ) and molar volume ( $V_2^0$ ), were taken or calculated from ref. 13.

The James-Martin pressure correction factor ( $J$ ) in eqn. 1 was calculated by using the equation

$$J = \frac{3}{2} \cdot \frac{(P_i/P_0)^2 - 1}{(P_i/P_0)^3 - 1} \quad (3)$$

As gas flow-rates and weights of stationary phases are very sensitive parameters for evaluating the activity coefficients at infinite dilution, they were determined with high accuracy. The flow-rates were checked at the beginning and end of each set of experiments at ambient temperature and were found to be highly consistent. The weights of stationary phases were checked before and after completing the entire set of experiments on a Mettler Model AE-100 balance measuring up to five decimal places. The loss in weight was found to be negligible.

## RESULTS AND DISCUSSION

The results for the limiting activity coefficients of all the aliphatic alcohols in DNDP at 15, 20 and 30% solvent loadings are reported in Tables I-III and for 15 and 30 solvent loadings of DIDP, DNBP and TCDBP in Tables IV-IX. In all instances the 30% loading indicates a regular decreasing trend in limiting activity coefficients. Although this trend was observed for the higher boiling solutes 1-pentanol, 1-butanol and 1-propanol even at 15% loading, methanol and ethanol deviated from this trend at 15% loading. The abnormal behaviour of these lower alcohols can be attributed to bulk and surface effects when the solvent loading is below 30%.

The quantitative interpretation of gas chromatographic data is often complicated by the occurrence of solute adsorption at one or more interfaces in the system.

TABLE I  
ACTIVITY COEFFICIENTS AT INFINITE DILUTION OF ALCOHOLS IN 13.7% DNDP

Solute	50°C	60°C	70°C	80°C	90°C	100°C
Methanol	1.90	1.86	2.32	2.55	2.61	3.15
Ethanol	1.76	1.55	1.57	1.82	2.08	2.07
1-Propanol	1.44	1.37	1.32	1.24	1.23	1.27
1-Butanol	1.37	1.32	1.25	1.18	1.07	1.01
1-Pentanol	1.23	1.18	1.11	1.04	0.99	0.89

TABLE II

ACTIVITY COEFFICIENTS AT INFINITE DILUTION OF ALCOHOLS IN 19.7% DNDP

<i>Solute</i>	<i>50°C</i>	<i>60°C</i>	<i>70°C</i>	<i>80°C</i>	<i>90°C</i>	<i>100°C</i>
Methanol	1.74	1.75	2.04	2.42	2.52	2.35
Ethanol	1.55	1.48	1.47	1.59	1.73	1.69
1-Propanol	1.53	1.35	1.26	1.20	1.16	1.24
1-Butanol	1.43	1.26	1.21	1.08	1.05	1.03
1-Pentanol	1.27	1.16	1.09	1.01	0.96	0.94

TABLE III

ACTIVITY COEFFICIENTS AT INFINITE DILUTION OF ALCOHOLS IN 29.8% DNDP

<i>Solute</i>	<i>50°C</i>	<i>60°C</i>	<i>70°C</i>	<i>80°C</i>	<i>90°C</i>	<i>100°C</i>
Methanol	2.31	2.12	2.14	2.09	2.07	1.99
Ethanol	1.91	1.77	1.69	1.61	1.54	1.46
1-Propanol	1.72	1.50	1.36	1.31	1.22	1.18
1-Butanol	1.72	1.48	1.34	1.18	1.11	1.05
1-Pentanol	1.52	1.26	1.16	1.08	1.04	0.97

TABLE IV

ACTIVITY COEFFICIENTS AT INFINITE DILUTION OF ALCOHOLS IN 14.8% DIDP

<i>Solute</i>	<i>50°C</i>	<i>60°C</i>	<i>70°C</i>	<i>80°C</i>	<i>90°C</i>	<i>100°C</i>
Methanol	2.06	2.05	2.46	2.81	2.93	2.79
Ethanol	1.98	1.83	1.83	1.82	2.08	2.05
1-Propanol	1.92	1.75	1.58	1.48	1.34	1.39
1-Butanol	1.80	1.56	1.46	1.31	1.21	1.16
1-Pentanol	1.53	1.38	1.30	1.19	1.11	1.08

TABLE V

ACTIVITY COEFFICIENTS AT INFINITE DILUTION OF ALCOHOLS IN 30.7% DIDP

<i>Solute</i>	<i>50°C</i>	<i>60°C</i>	<i>70°C</i>	<i>80°C</i>	<i>90°C</i>	<i>100°C</i>
Methanol	2.45	2.32	2.35	2.30	2.23	2.16
Ethanol	2.22	2.05	1.89	1.79	1.73	1.64
1-Propanol	1.93	1.73	1.58	1.46	1.36	1.29
1-Butanol	1.86	1.67	1.49	1.36	1.25	1.15
1-Pentanol	1.52	1.37	1.30	1.29	1.20	1.13

TABLE VI

ACTIVITY COEFFICIENTS AT INFINITE DILUTION OF ALCOHOLS IN 15.1% DNBP

<i>Solute</i>	<i>50°C</i>	<i>60°C</i>	<i>70°C</i>	<i>80°C</i>	<i>90°C</i>	<i>100°C</i>
Methanol	2.07	2.01	2.05	2.02	2.01	2.08
Ethanol	2.00	1.76	1.66	1.68	1.65	1.60
1-Propanol	1.86	1.63	1.41	1.31	1.26	1.25
1-Butanol	1.78	1.58	1.44	1.29	1.24	1.13
1-Pentanol	1.64	1.46	1.29	1.20	1.14	1.06

TABLE VII

ACTIVITY COEFFICIENTS AT INFINITE DILUTION OF ALCOHOLS IN 30.6% DNBP

<i>Solute</i>	<i>50°C</i>	<i>60°C</i>	<i>70°C</i>	<i>80°C</i>	<i>90°C</i>	<i>100°C</i>
Methanol	2.53	2.43	2.42	2.38	2.37	2.31
Ethanol	2.19	2.68	2.02	1.98	1.94	1.88
1-Propanol	2.05	1.81	1.67	1.59	1.55	1.53
1-Butanol	2.00	1.89	1.69	1.56	1.43	1.39
1-Pentanol	2.01	1.61	1.48	1.39	1.29	1.27

TABLE VIII

ACTIVITY COEFFICIENTS AT INFINITE DILUTION OF ALCOHOLS IN 13.1% TCDBP

<i>Solute</i>	<i>50°C</i>	<i>60°C</i>	<i>70°C</i>	<i>80°C</i>	<i>90°C</i>	<i>100°C</i>
Methanol	3.49	3.97	4.85	5.17	4.18	3.82
Ethanol	3.22	3.11	3.08	3.38	3.37	3.00
1-Propanol	2.89	2.73	2.43	2.26	2.18	2.17
1-Butanol	2.85	2.61	2.28	2.03	1.84	1.76
1-Pentanol	2.45	2.27	2.02	1.83	1.69	1.72

TABLE IX

ACTIVITY COEFFICIENTS AT INFINITE DILUTION OF ALCOHOLS IN 30.9% TCDBP

<i>Solute</i>	<i>50°C</i>	<i>60°C</i>	<i>70°C</i>	<i>80°C</i>	<i>90°C</i>	<i>100°C</i>
Methanol	3.63	3.89	4.02	4.01	3.99	3.88
Ethanol	2.93	2.72	2.61	2.58	2.48	2.34
1-Propanol	2.72	2.59	2.63	2.44	2.09	2.03
1-Butanol	2.61	2.29	2.11	1.93	1.78	1.67
1-Pentanol	2.35	2.05	1.84	1.71	1.59	1.50

TABLE X  
SPECIFIC RETENTION VOLUMES ( $V'_g$ ) OF ALCOHOLS IN DNNDP

$W_1$  = weight of DNNDP at 13.7% loading (0.3873 g);  $W_2$  = weight of DNNDP at 19.7% loading (0.6429 g);  $W_3$  = weight of DNNDP at 29.8% loading (0.9362 g);  $1/W_1 = 2582$  (kg);  $1/W_2 = 1555$  (kg);  $1/W_3 = 1068$  (kg).

Temperature (°C)	Methanol			Ethanol			i-Propanol			i-Butanol			i-Pentanol		
	$1/W_1$	$1/W_2$	$1/W_3$	$1/W_1$	$1/W_2$	$1/W_3$	$1/W_1$	$1/W_2$	$1/W_3$	$1/W_1$	$1/W_2$	$1/W_3$	$1/W_1$	$1/W_2$	$1/W_3$
50	0.050	0.055	0.042	0.103	0.115	0.093	0.296	0.278	0.248	0.744	0.817	0.679	2.219	2.142	1.795
60	0.033	0.036	0.030	0.072	0.075	0.063	0.173	0.189	0.170	0.501	0.502	0.458	1.254	1.274	1.173
70	0.018	0.021	0.020	0.028	0.049	0.043	0.121	0.126	0.117	0.304	0.323	0.291	0.770	0.780	0.733
80	0.012	0.013	0.014	0.029	0.031	0.030	0.083	0.086	0.079	0.212	0.221	0.197	0.491	0.504	0.473
90	0.008	0.008	0.011	0.017	0.019	0.022	0.056	0.059	0.056	0.144	0.147	0.136	0.322	0.332	0.313
100	0.005	0.006	0.008	0.012	0.014	0.016	0.037	0.038	0.040	0.100	0.098	0.094	0.230	0.220	0.213

Solid supports do interact, but they are made inert to most of the solutes. Interactions on the other surfaces cause serious errors. Martin<sup>14</sup> was the first to point out that solute adsorption on the surface of a bulk liquid could markedly affect the retention volumes in gas-liquid partition chromatographic (GLPC) systems. This was further supported by Pecsok *et al.*<sup>15</sup> and directly substantiated by static measurements by Martire *et al.*<sup>16,17</sup>, who used a polar stationary phase to assess the Gibbs adsorption effects, which occur only with such solvents. Martire<sup>18</sup> further observed that with certain polar solute-polar solvent systems in which the solute activity coefficients were only around unity, liquid surface excess effects do occur. Pecsok and Gump<sup>19</sup> applied a static method to polar solutes in a non-polar solvent, squalene, and showed that a considerable contribution to the retention volume from Gibbs adsorption effects affected the GLPC system.

Conder *et al.*<sup>20</sup> developed equations for the study of the Gibbs effect. These theoretical equations were further substantiated<sup>21</sup> with the help of experimental data for C<sub>3</sub>-C<sub>5</sub> alcohols in squalene.

When there are no surface effects, the net retention volume ( $V_N$ ) of a solute is generally represented by the equation<sup>22</sup>

$$V_N = K_R V_L \quad (4)$$

where  $K_R$  is the solute liquid-gas partition coefficient and  $V_L$  is volume of the stationary phase. When gas-liquid interfacial adsorption contributes to retention, eqn. 4 is expanded to

$$V_N = K_R V_L + K_S A_L \quad (5)$$

where,  $A_L$  is the liquid-phase surface area,  $V_N$  is the net retention volume and  $K_S$  is the solute liquid-gas interfacial adsorption partition coefficient. The bulk partition coefficient,  $K_R$ , is found by plotting  $V_N/V_L$  versus  $1/V_L$  and extrapolating it to the ordinate. Alternatively, plots can also be made of  $V_g^0$  vs.  $1/W$  as  $V_N/V_L = V_N \rho_L / W = V_g^0 \rho_L$  and  $1/V_L = \rho_L / W$ , where  $\rho_L$  is the density of stationary phase in m<sup>3</sup>/kg.

In these studies, the specific retention volumes of the aliphatic alcohols were evaluated in DNNDP stationary phase at column loadings of 13.7, 19.7 and 29.8% at 50, 60, 70, 80, 90 and 100°C. The results are presented in Table X.  $V_g^0$  was plotted vs.  $1/W$  and extrapolated to the ordinate to evaluate the real specific retention volume. Eqns 4 and 5 can be written in terms of  $V_g^0$  as

$$V_g^0 \rho_L = K_{R \text{ obsd.}} \quad (6)$$

where  $K_{R \text{ obsd.}}$  is the apparent distribution coefficient evaluated from the experimental retention volume data, and

$$V_g^0 \rho_L = \frac{A_L K_S \rho_L}{W} + K_R \quad (7)$$

The real  $K_R$  values and hence the real  $\gamma_2^\infty$  values can be evaluated from the extrapolated  $V_g^0$  values, which are the intercepts at the ordinate ( $1/W = 0$ ). Typical

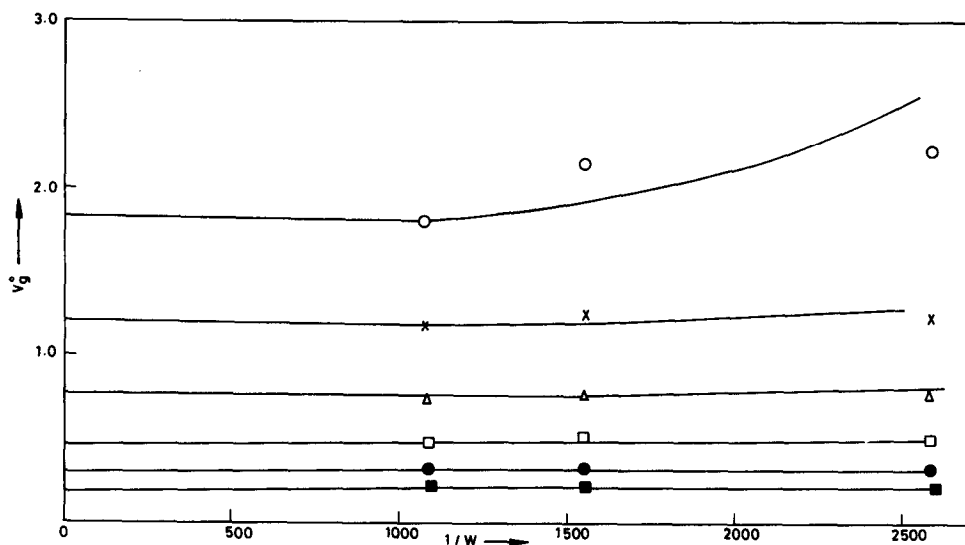


Fig. 1. Specific retention volume of 1-pentanol vs. reciprocal of weight of DNDP. ○ = 50°C; × = 60°C; △ = 70°C; □ = 80°C; ● = 90°C; ■ = 100°C.

plots are given in Fig. 1 for 1-pentanol at 50, 60, 70, 89, 90 and 100°C. Similar trends are observed for the other aliphatic alcohols.

The limiting activity coefficients were calculated from these specific retention volumes. The density of DNDP was determined at 25°C to be 1.0083 g/ml.

The real  $V_g^0$  values and  $\gamma_2^\infty$  values are presented in Table XI. They are in excellent agreement with the experimentally observed values presented in Table III. This exercise clearly establishes that the limiting activity coefficients of these aliphatic alcohols are most reliable and accurate. This confirms the work of Martire *et al.*<sup>16</sup>, who ascertained that with low-loaded columns surface effects predominate over solubility.

No direct information is available in the literature on the activity coefficients of these alcohols with respect to any phthalate stationary phase. Keulemans<sup>23</sup> evaluated activity coefficients at infinite dilution with respect to DIDP from partition coefficient data<sup>3</sup>. These values were reported at 75, 95, 105, 115 and 135°C. The activity coefficients at infinite dilution as calculated by Keulemans are not in very good agreement with those obtained here, for specific reasons. In their work<sup>3</sup>, the specific retention volume was calculated without making a correction for the dead volume as specified in eqn. 1 in this paper. In the reported work, the gas flow-rates were measured at the column temperature without any temperature corrections for ambient conditions. Moreover, the gas-phase fugacity corrections as indicated in eqn. 2 were not applied to the reported data.

The data in Tables I–IX reveal the following effects:

(a) Effect of molecular weight of alcohols: there is a steep fall in the activity coefficients at infinite dilution with increase in the molecular weight of the alcohols. In all instances the activity coefficients at infinite dilution are highest for methanol and lowest for pentanol.



TABLE XI

REAL SPECIFIC RETENTION VOLUMES ( $V_g^0$ ) AND ACTIVITY COEFFICIENTS AT INFINITE DILUTION OF ALCOHOLS IN DNDP

Solute	50°C		60°C		70°C		80°C		90°C		100°C	
	$V_g^0$	$\gamma_2^\infty$	$V_g^0$	$\gamma_2^\infty$	$V_g^0$	$\gamma_2^\infty$	$V_g^0$	$\gamma_2^\infty$	$V_g^0$	$\gamma_2^\infty$	$V_g^0$	$\gamma_2^\infty$
Methanol	0.041	2.31	0.029	2.16	0.020	2.20	0.014	2.19	0.011	2.06	0.007	2.17
Ethanol	0.091	1.94	0.062	1.80	0.042	1.72	0.030	1.63	0.022	1.56	0.016	1.49
1-Propanol	0.240	1.77	0.170	1.51	0.110	1.44	0.078	1.32	0.052	1.32	0.039	1.21
1-Butanol	0.680	1.71	0.479	1.40	0.299	1.30	0.190	1.26	0.139	1.10	0.091	1.09
1-Pentanol	1.842	1.47	1.220	1.21	0.809	1.06	0.480	1.06	0.308	1.02	0.210	0.98

(b) Effect of temperature: there is a regular decrease in the limiting values for all the alcohols with increasing temperature when 30% solvent loadings are considered. Only methanol shows a peculiar behaviour; the limiting values first increase from 50 to 70°C and finally show a slight decrease. The natural logarithm of the activity coefficients at infinite dilution increases with decreasing temperature, and they converge towards a closer value at higher temperatures. On plotting these values *versus*  $1/T$ , non-linear behaviour is observed (Figs. 2-5).

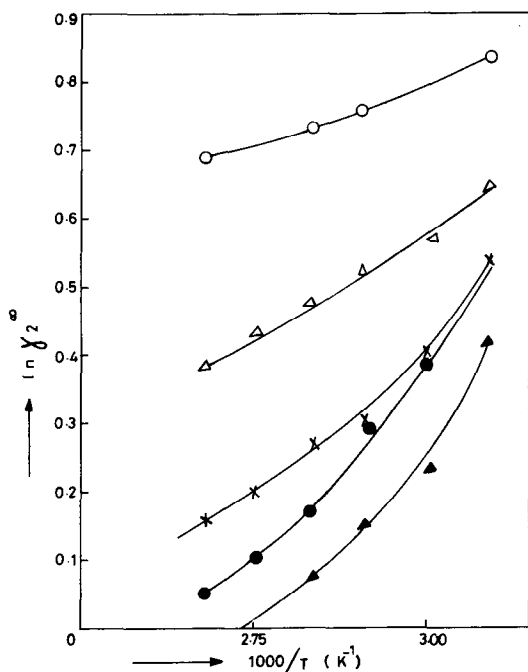


Fig. 2. Activity coefficients at infinite dilution ( $\gamma_2^\infty$ ) of (○) methanol, (Δ) ethanol, (×) 1-propanol, (●) 1-butanol and (▲) 1-pentanol in DNDP with a 29.8% column loading.

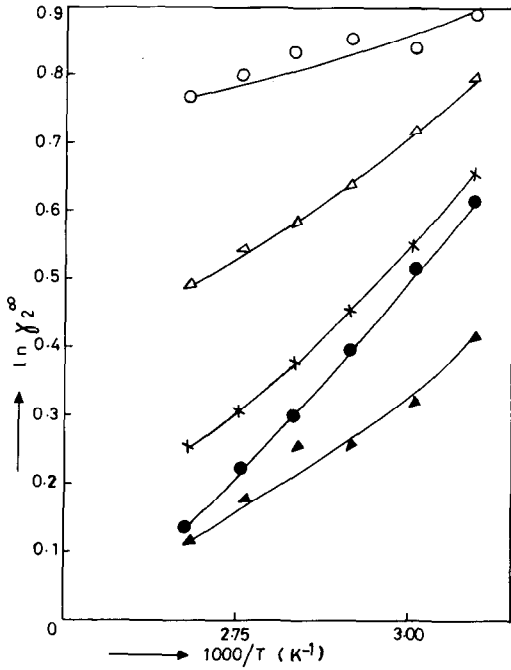


Fig. 3. Activity coefficients at infinite dilution ( $v_2^\infty$ ) of (○) methanol, (△) ethanol, (×) 1-propanol, (●) 1-butanol and (▲) 1-pentanol in DIDP with a 30.7% column loading.

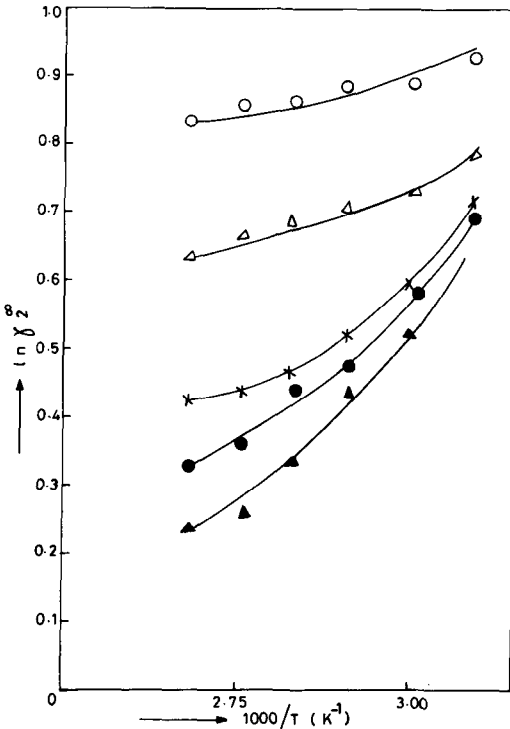


Fig. 4. Activity coefficients at infinite dilution ( $v_2^\infty$ ) of (○) methanol, (△) ethanol, (×) 1-propanol, (●) 1-butanol and (▲) 1-pentanol in DNBP with a 30.6% column loading.

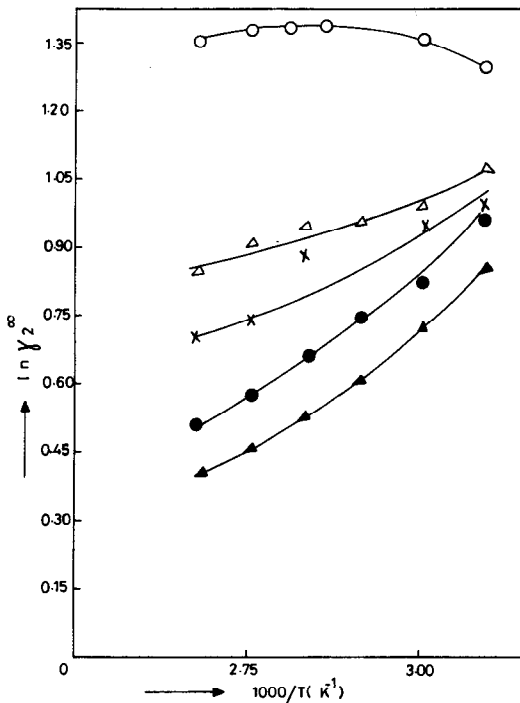


Fig. 5. Activity coefficients at infinite dilution ( $\gamma_2^\infty$ ) of (○) methanol, (Δ) ethanol, (×) 1-propanol, (●) 1-butanol and (▲) 1-pentanol in TCDBP with a 30.9% column loading.

(c) Departure from Raoult's law: the interaction parameters ( $\gamma_2^\infty$ ) of highly pure polar solutes with mild polar solvents do not show a significant deviation from Raoult's law. The maximum deviation occurs with TCDBP. In almost all instances the deviation is positive. The higher boiling alcohols in some instances show a negative deviation at higher temperature.

#### SYMBOLS

$B_{22}$	second virial coefficient, m <sup>3</sup> /mol
$F_m$	flow-rate of carrier gas, m <sup>3</sup> /s
$J$	James–Martin pressure correction factor
$M_1$	molar mass of stationary phase, kg/mol
$P_i$	pressure at the inlet of column, Pa
$P_0$	pressure at the outlet of column, Pa
$P_{H_2O}$	water vapour pressure at $T_m$ , Pa
$P_2^0$	vapour pressure of solute (component 2), Pa
$R$	gas constant, 8.314 J/mol · K
$T_m$	ambient temperature, K
$t_r$	retention time of solute, s
$t_0$	retention time of an inert compound, s
$T_{exp}$	column temperature, K

- $V_2^0$  molar volume of solute (component 2) at  $T_{\text{exp}}$ ,  $\text{m}^3/\text{mol}$   
 $W$  mass of stationary phase, kg  
 $\gamma_2^\infty$  activity coefficient of solute (component 2) at infinite dilution.

#### ACKNOWLEDGEMENTS

The authors extend their appreciation to Dr. Asad Ali Khan, Head, Chemical Engineering Division, RRL, Hyderabad, for his encouragement in carrying out this work and Mr. V. S. N. Murthy, for typing the manuscript.

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