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ISOTHERMAL VAPOUR-LIQUID EQUILIBRIA DATA OF METHANOL + PROPAN-2-OL, METHANOL + 2 - METHYL PROPAN-2-OL AND PROPAN-2-OL + 2-METHYLPROPAN-2-OL BINARY MIXTURES AT 333.15K

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ABSTRACT

The vapour-liquid equilibria (VLE) data of methanol + propan-2-ol + 2-methylpropan-2-ol binary mixtures are investigated at 333.15k, using gas chromatographic technique. For binary mixtures, the total pressure, the compositions of the components in the vapour phase are obtained from the instrument and these data are then used to calculate the second virial coefficients of pure components to account for the deviations of these mixtures from ideal solution behaviour. The excess Gibbs free energies of mixing for these binary systems are then determined. The y-x plots reveals that the mixtures methanol + propan-2-ol and methanol +2-methylpropan-2-ol deviate strongly from ideal solution behaviour. The excess Gibbs free energies (ΔG^E) of mixing for these binary systems are negative quantities, confirming negative deviations from ideality. Minimum ΔG^E value of 450 J.mol^{-1} is obtained for methanol + 2-methylpropan-2-ol mixtures at 0.45 mole fraction of methanol. Methanol + propan-2-ol mixtures exhibit a minimum ΔG^E value of 100 J mol^{-1} at 0.5 mole fraction of methanol. The least minimum ΔG^E value of 15 J. mol^{-1} is obtained for propan-2-ol +2-methyl propan-2-ol mixtures at 0.5 mole fraction of propan-2-ol. The consistency of these data is verified using Wilson's model for calculating ΔG^E values. The calculated change in Gibbs free energies (ΔG^E_{calc}) obtained were in good agreement with the experimentally determined ΔG^E values.

KeyWords: VLE, Spectrometric, Deviation, Excess, Ideality.

INTRODUCTION

The VLE data of interest are usually the liquid (x) and the vapour compositions (y), activity of the components (f) and the excess Gibbs free energies (ΔG^E) of the mixtures. The total pressure (P_T) of the mixtures are also important.

The two most important techniques for the investigation of the VLE of metallic systems are mass spectrometric and emf methods (Kubaschewski and Alcock, 1979). Metals generally have low vapour pressures and their vapour mixtures approximate to ideal solutions. Mass spectrometric method yields accurate data of the components of the metallic systems. Diffusional delay is the major problem associated with the emf technique. It is best used for the conductive-liquid metal systems. Direct vapour pressure measurement has been the method for obtaining VLE data of organic liquid mixtures.

Differential oil-mercury manometer technique (Kubascheski and Alcock, 1979) has been used for this purpose in recent years. These methods are used to measure the total pressure of the liquid mixtures. Methods for the degassing of organic liquid mixtures, have been reported in the literature (Apelblat et al, 1980). Some of these techniques are unable to provide the compositions of the components in the vapour phase.

Dal Nagore and Juvet Jr., (1966) reported that gas chromatographic method provides the VLE data for organic liquid mixtures easily. Kolb (1975) demonstrated the application of gas chromatography for measuring activity coefficients of binary mixtures. In a typical chromatogram of a vapour phase of the binary mixtures, the compositions of the components can be obtained from the peak areas of the components. These peak areas are proportional to the partial pressures of these components. Through calibration the total pressure, P_T, of the mixtures can be obtained.

The aim of this paper is to illustrated the usefulness of the gas chromatographic technique for obtaining VLE data of liquid mixtures. In chemical process industries, fluid mixtures are often separated into their components by diffusional separations such as distillation, absorption and extraction. The design of such separation operations require quantitative estimates of the partial equilibrium properties of fluid mixtures. The knowledge of the VLE data of mixtures is important for chemical and petrochemical process,

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as well as for the understanding of the physical state of the molecules in the mixtures.

Moreover, Prezeiji (1987) reported that methanol, propan-2-ol and 2-methylpropan-2-ol are good octane boosters in gasoline refining. Information is lacking on the VLE data of these alcohols in the literature. Only few reports are available on binary systems of carboxylic acids with a non-polar component.

EXPERIMENTAL TECHNIQUES

Varian 3700 model of gas-liquid chromatograph with spectra physics integrator (SP 4270) was used to determine the VLE data of the mixtures of methanol, propan-2-ol and 2-metylpropan-2-ol as described by Kolb (1975). The equipment has a flame ionization detector, with a stainless steel column packed with chromosorb 102 of between 60 to 80 mesh. The temperature of the column was maintained at 170°C. The equipment's data reproducibility was within ± 2 percent.

Absolute methanol, propan-2-ol and 2-methylpropan-2-ol were supplied by East Anglia chemicals, British Drug House (BDH) and May and Baker respectively. Specific gravity, refractive indices and boiling points of these alcohols were measured to check the purity of each sample.

The mixtures to be studied were prepared by measuring both components of each binary mixtures and the concentrations in mole fractions (x) calculated and tabulated (Tables, 1, 2, and 3) 2ml of each o

Table 1: Isothermal Vapour-Liquid Equilibria (VLE) of methanol (1) + propan-2-ol mixtures at 333.15k

X_1	P_T (mm hg)	y_1	f_1	f_2	$-\Delta G^E$	$-\Delta G^E_{calc.}$
0.0000	312.0	0.0000	-	-	-	-
0.1236	314.9	0.2029	0.8732	0.9994	47.09	49.21
0.1989	362.9	0.3160	0.9096	0.9961	60.87	70.35
0.2509	377.5	0.3885	0.9111	0.9934	78.44	81.42
0.3093	395.1	0.4644	0.9255	0.9320	94.47	98.21
0.3914	420.9	0.5612	0.9428	0.9820	94.47	98.21
0.4462	438.8	0.6196	0.9528	0.9768	95.76	100.00
0.5708	480.9	0.7356	0.9712	0.9636	90.28	95.19
0.7276	535.7	0.8531	0.9872	0.9442	69.28	73.36
0.8445	577.4	0.9237	0.9948	0.9294	43.73	46.96
0.9505	615.3	0.9776	0.9988	0.9164	15.13	16.33
1.0000	633.0	1.0000	-	-	-	-

$\Lambda_{12} = 0.68409$; $\Lambda_{21} = 1.55189$; $\overline{V_1^0}$ 41.00783 cm^3mol^{-1}; $\overline{V}_2^0 = 75.06220$ cm^3mol^{-1};

$\beta_{11} = -1053.8479$ cm^3mol^{-1}; $\beta_{22} = -1739.10451$ cm^3mol^{-1}.

1 represents methanol

2 represents propan-2-ol

these mixtures was transferred with a pipette into 5ml. Sample tubes tightly fitted with a rubber-septum. These tubes were arranged on the rack and kept for 50 minutes to 60 minutes in a thermoregulator at 333.15k. After the equilibrium of the volatile components between gas and liquid phases had been established an aliquot of the vapour phase content, above the liquid mixture was withdrawn with a gas string and transferred immediately to the gas chromatograph. The peak areas, retention time and mole percentage of the components of the vapour phase were estimated by the integrator. The experiment was repeated with each of the pure solvents and their peak areas obtained.

RESULTS AND DISCUSSIONS

In the gas chromatographic technique, the peak area of a component in a mixture is proportional to the partial pressure of the component. The standards are the pure solvents. By calibration using the pure solvents, the proportionality constant can be obtained and used to evaluate the partial pressure of a component in a mixture. For a binary mixture, the total pressure, P_T, is the sum of the partial pressure of the components 1 and 2 i.e $P_1 + P_2$. The compositions of components 1 and 2 in the vapour phase are Y_1 and Y_2, which are the ratios P_1/P_T and P_2/P_T. P_T and y_1 and y_2, the mole fractions of components 1 and 2 in the vapour phase, are obtained from the equipment.

Some vapour mixtures deviate from ideal gas behaviour and the deviations from ideality can be

Table 2: Isothermal Vapour-Liquid Equilibria (VLE) data of methanol + 2-methyl-propan-2-ol at 333.15k.

X_1	P_T (mm hg)	y_1	f_1	f_3	$-\Delta G^E$	$-\Delta G^E_{calc.}$
0.0000	303.00	0.0000	-	-	-	-
0.0561	301.6	0.0569	0.4739	0.9944	130.72	126.97
0.1435	306.8	0.1786	0.5929	0.9714	276.61	270.60
0.1865	312.8	0.2473	0.6443	0.9560	328.47	321.29
0.2468	325.0	0.3464	0.7091	0.9329	379.89	373.85
0.3129	342.6	0.4521	0.7699	0.9053	415.97	410.02
0.4054	373.4	0.5849	0.8395	0.8665	432.44	429.06
0.5194	418.2	0.7179	0.9029	0.8197	411.61	411.02
0.6741	485.8	0.8483	0.9583	0.7603	326.90	328.83
0.7250	508.9	0.8809	0.9705	0.7428	286.61	289.84
0.8082	546.8	0.92.59	0.9800	0.7147	223.67	215.29
0.9545	612.8	.08854	0.9984	0.6697	54.76	55.97
1.000	633.0	1.0000	-	-	-	-

$\wedge_{12} = 0.47720$; $\wedge_{21} = 2.65903$; $\overline{V_1^0}$ 41.00783 cm^3mol^{-1}; $\overline{V}_3^0 = 94.05094\ cm^3mol^{-1}$;

$\beta_{11} = -1053.8479\ cm^3mol^{-1}$; $\beta_{33} = -2019.56742\ cm^3mol^{-1}$.

1 represents methanol

3 represents 2-methyl propan-2-ol

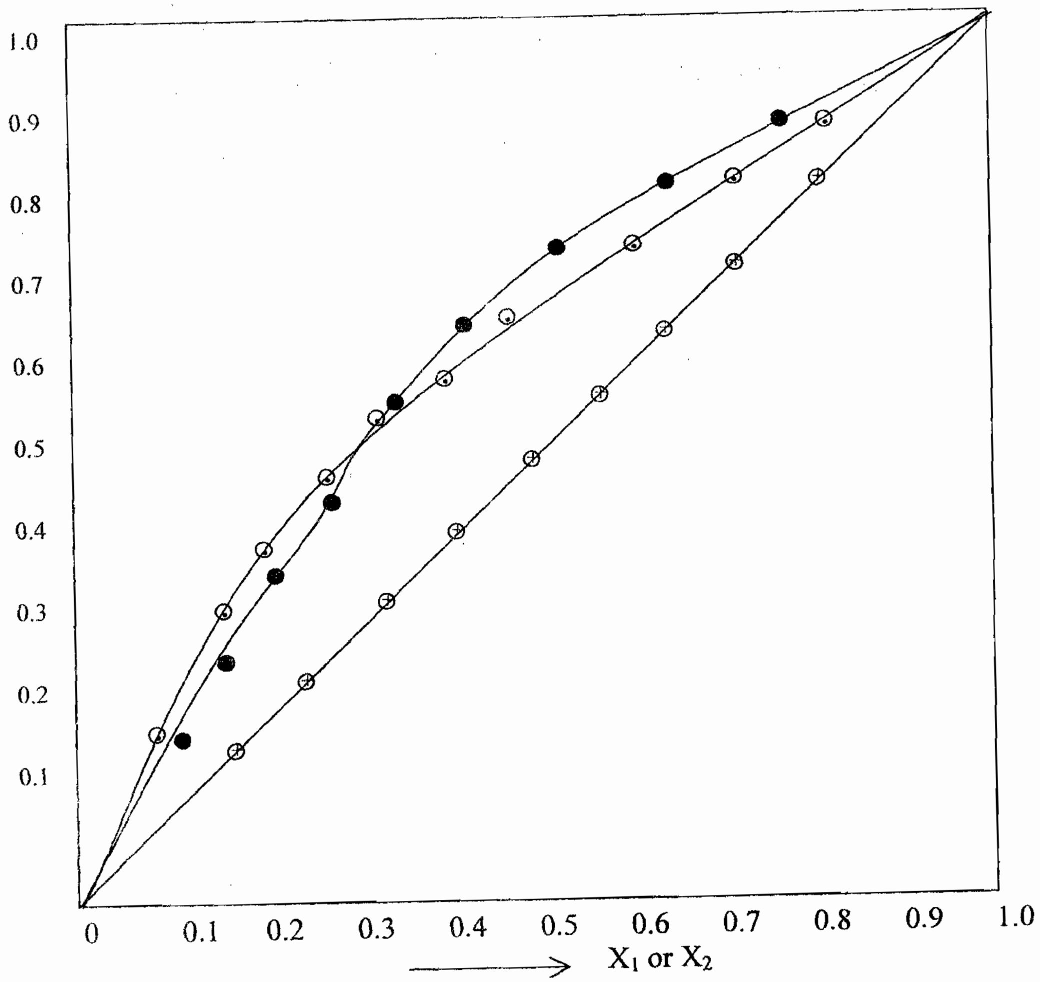


Fig 1: Y – X data for the alcohol mixtures at 333.15K.

KEY

⊙ = Y – X data for methanol – propan-2-ol mixtures
● = Y – D data for methanol –2-methyl propan-2-ol mixtures.
⊕ = Y – X data for propan-2-ol – 2 methyl propan-2-ol mixture

1 represents methanol
2 represents propan-2-ol

treated by introducing the second Virial coefficients β_{11} and β_{22} (McGlashan, 1979). From the knowledge of total pressure, P_T, the vapour compositions Y_1 and Y_2, the second Virial coefficients can be evaluated, using the model first introduced by Van Ness (1964).

$$\ln f_1 = \ln\left(\frac{Y_1 P_T}{X_1 P_1^0}\right) + \left[\frac{\left(B_{11} - \overline{V}_1^0\right)\left(P_T - P_1^0\right)}{RT}\right] + \frac{(1 - Y_1)^2 .2\, \delta_{12} P_T}{RT} \qquad (1)$$

Where $\overline{V}_1^0$ and P_1^0 are the molar volume and vapour pressure of pure component 1 respectively. R is the gas constant and T is the temperature in degree Kelvin. δ_{12} is the third virial coefficient which is very low for

the mixtures studied and was not used in evaluating activity coefficient (f).
Apelblat et. al (1980) used this expression to study associated solutions. The alcohol mixtures studied are associated through hydrogen bonding, in a linear fashion.

$$CH_3 - O - H \cdots H - O - CH - (CH_3)_2.$$

Methanol H-bonding Propan-2-ol

The excess Gibbs free energies (ΔG^E) are calculated using the relationship.

$$\Delta G^E = RT\,(x_1 \ln f_1 + x_2 \ln f_2) \qquad (2)$$

The consistency of the data is tested utilizing Wilson's model for calculating ΔG^E values. The expression in given by equation (3).

$$\frac{\Delta G^E}{RT} = (x_1 \ln (x_1 + \Lambda_{12} x_2) - x_2 \ln (x_2 + \Lambda_{21} x_1))$$

Using this equation and ΔG^E values obtained experimentally, the Wilson's constants Λ_{12} and Λ_{21} are obtained. These constants are then used to calculate excess Gibbs free energies (ΔG^E_{calc})

The results obtained are summarized in tables 1, 2, and 3 and figures 1 and 2. The liquid compositions (x), compositions of the vapour phase (Y), total pressure (P_T), activity coefficients (f), the

Table 3: Isothermal Vapour-Liquid Equilibria (VLE) of propan-2-ol+2-methylpropan-2-ol mixture at 333.15K.

x_2	P_T (mm hg)	y_2	f_2	F_3	$-\Delta G^E$	$-\Delta G^E_{calc.}$
0.0000	312.0	0.0000	-	-	-	-
0.1460	309.8	0.1408	0.9839	0.9992	8.474	8.001
0.1909	309.2	0.1842	0.9852	0.9989	10.351	9.939
0.2608	308.3	0.2530	0.9875	0.9982	12.775	12.502
0.3922	306.7	0.3839	0.9911	0.9959	16.628	015.692
0.4796	305.9	0.4718	0.9934	0.9945	16.746	16.594
0.5528	305.2	0.5460	0.9951	0.9924	16.971	16.577
0.6309	304.6	0.6253	0.9965	0.9903	16.092	15.758
0.7088	304.0	0.7048	0.9977	0.9869	15.157	14.097
0.8255	303.5	0.8235	0.9992	0.9831	10.068	9.978
0.9465	303.1	0.9461	0.9999	0.9779	3.574	3.561
1.0000	303.0	1.000	-	-	-	-

$\Lambda_{23} = 1.14973$; $\Lambda_{32} = 0.88322$; $\overline{V}^0_2 = 75.06220 cm^3mol^{-1}$; $\overline{V}^0_3 = 94.05094\ cm^3mol^{-1}$;

$\beta_{22} = -1739.10451\ cm^3mol^{-1}$; $\beta_{33} = -2019.56742\ cm^3mol.^{-1}$

2 represents propan-2-ol

3 represents 2-methyl propan-2-ol

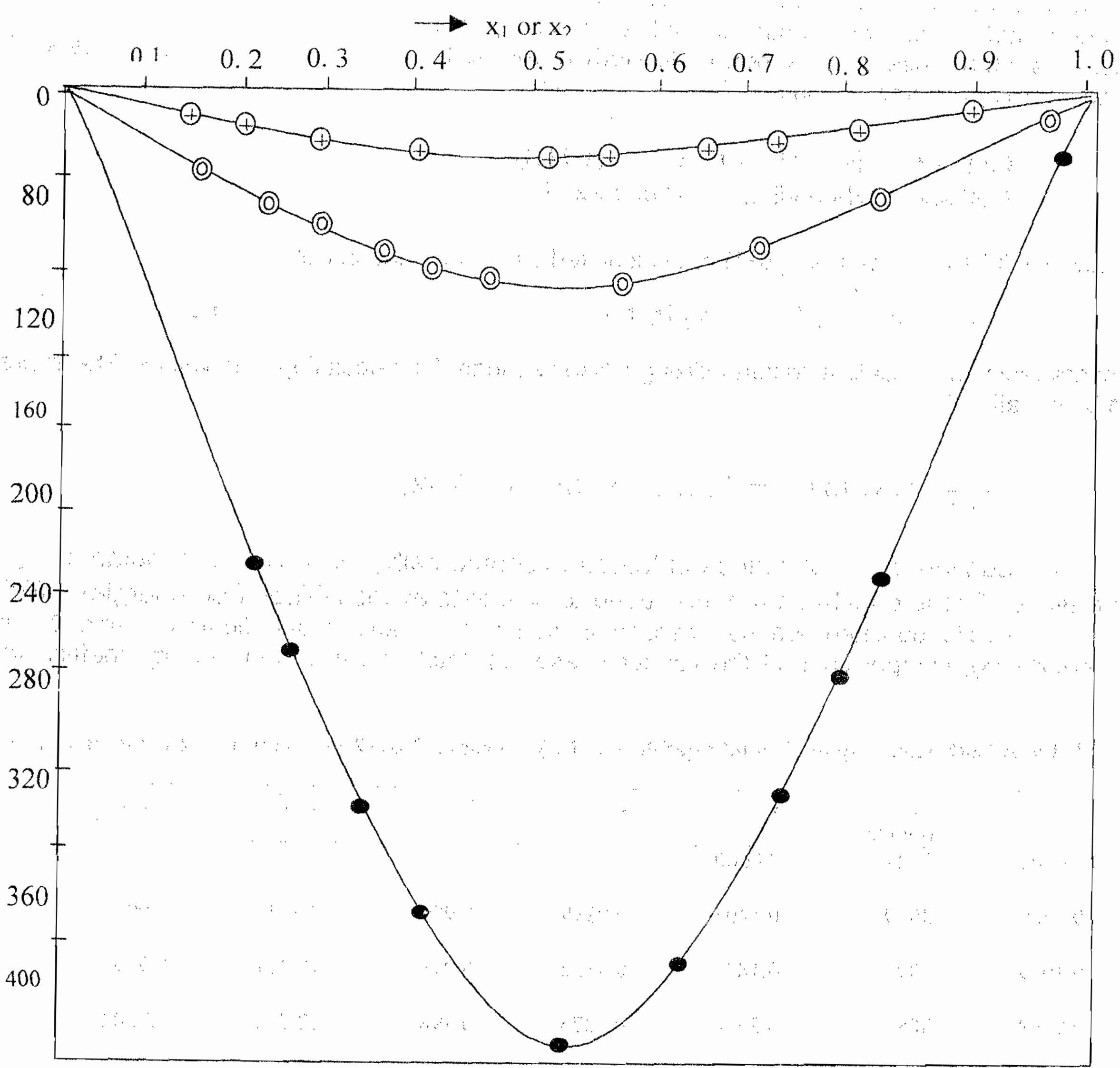


Fig.2: The dependence of Excess Gibbs Energies ΔG^E of mixing of the alcohol mixtures at 333.15k on composition.

KEY

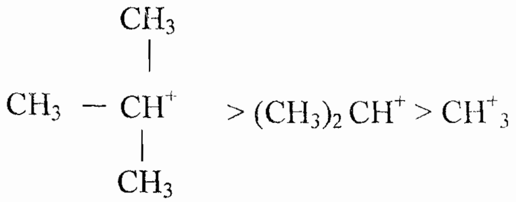
● = ΔG^E values of methanol + 2 methyl-propan-2-ol mixture
◎ = ΔG^E values of methanol + popan-2-ol mixture
⊕ = ΔG^E values of propan-2-ol + 2 methyl propan-2-ol mixture

1 represents methanol
2 represents propan-2-ol

excess Gibbs free energies (ΔG^E) and calculated excess Gibbs free energies ($\Delta G^E_{calc.}$) are contained in the tables. The tables also show the second virial coefficients (β), the molar volumes (V_1^0) and the Wilson's constants (Λ).

The values of the specific gravity, refractive index and boiling points of the absolute alcohols are in agreement with the literature values within ± 2 percent, which is the sort of error observed in the measurements.

The y-x plots (fig 1) indicate the two of the mixtures deviate strongly from ideal solution behaviour. The y-x data of propan-2-ol + 2-methylpropan-2-ol exhibit almost an ideal behaviour. Since for an ideal behaviour, vapour compositions are equal to the liquid compositions and the y – x plot is linear (fig 1). The excess Gibbs free energies are negative quantities suggesting negative deviation from ideality due to molecular association through hydrogen bonding (fig 2). Minimum ΔG^E value of 450 J. mol^{-1} is obtained for methanol + 2-methylpropan-2-ol mixtures at 0.45 mole fraction of methanol. Methanol + propan-2-ol mixtures exhibit a minimum ΔG^E value of 100 $J.mol^{-1}$ at about 0.5 mole fraction of methanol. The least minimum ΔG^E value of 18 J. $mole^{-1}$ is obtained for propan-2-ol + 2-methyl propan-2-ol mixtures at 0.5 mole fraction of propan-2-ol (Fig 2). The highest the negative ΔG^E value, the more stable the mixture is. Therefore these data suggest that methanol + 2-methylpropan-2-ol mixtures are the most stable. The observed stability follows the order of the stability of the carbonium ions of these alcohols. The stability decreases in the order.



$$\mathrm{CH_3} - \overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{CH^+}}} > (\mathrm{CH_3})_2\,\mathrm{CH^+} > \mathrm{CH^+_3}$$

due to +1 inductive effect of the methyl groups. The bond between methanol and 2-methyl propan-2-ol is stronger than the bond between methanol and propan-2-ol. The bond between propan-2-ol and 2-methylpropan-2-ol is the weakest probably due to steric hindrance and the mixtures approximate to ideality. This is illustrated by the least ΔG^E value (tables 1, 2 and 3).

CONCLUSION

VLE data of organic mixtures can be determined using gas chromatographic method by measuring peak area of the components in the vapour phase. This technique is used to determine the VLE data of methanol, propan-2-ol and 2-methylpropan-2-ol binary mixtures. The vapour compositions (y), liquid compositions (x) and the total vapour pressures (P_T) of the mixtures are used to compute activity coefficients (f) and excess Gibbs free energies.

The ΔG^E values are negative quantities, indicating negative deviation from ideal solution behaviour. Wilson's model was used to check the consistency of these data by calculating ΔG^E_{calc} values. Methanol +2-methylpropan-2-ol system has a minimum ΔG^E value of 450 J. mol^{-1}, followed by methanol + propan-2-ol system with 100 J. mol^{-1}. Propan-2-ol + 2-methyl propan-2-ol system has the least minimum ΔG^E value of 18 $J.mol^{-1}$.

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APPENDIX: Glossary of symbols

VLE	Vapour-liquid Equilibria
$X_{1,2}$	Liquid composition of component 1 or 2 (in mole fraction)
$Y_{1,2}$	Vapour composition of component 1 or 2 (in mole fraction)
P_T	Total vapour pressure of the liquid mixtures
$P_{1,2}$	Partial vapour pressure of component 1 or 2.
$P^0_{1,2}$	Vapour pressure of pure component 1 or 2.
β_{11} or β_{22}	Second virial coefficients of pure component 1 or 2.
$\overline{V}^0_{1,2}$	Molar volume of pure component 1 or 2
$\Lambda_{1,2}$	Wilson's equation constant
$f_{1,2}$	Activity coefficient of component 1 or 2
ΔG^E	Change in excess Gibbs free energy
ΔG^E_{calc}	Calculated change in excess Gibbs free energy.