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PHASE EQUILIBRIA FOR BINARY MIXTURES OF NONANE WITH OCTANE AND OCTANE WITH ORTHOXYLENE, METAXYLENE AT 101.3 kPa

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ABSTRACT

Isobaric vapour-liquid equilibrium boiling temperature measurements have been determined at 101.3 kPa as function of composition for the binary mixtures of nonane with octane and octane with orthoxylene and metaxylene by using a recirculation type apparatus. The experimental temperature, vapour and liquid composition (T-x-y) results were correlated with the NRTL and UNIQUAC models. All systems studied here behave like non-ideal solutions.

KEYWORDS

Nonane, Octane, Orthoxylene, Metaxylene, Isobaric, Vapour liquid equilibrium and Binary.

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INTRODUCTON

Experimental data of excess thermodynamic properties of liquids and liquid mixtures are of great fundamental and practical importance. These properties allow one to draw information on the structure and interactions of mixed solvents. The knowledge of phase equilibrium properties of liquid mixtures are fascinating and of great fundamental, practical importance, and industrial points of view. An accurate and complete knowledge of VLE data on the mixtures under consideration is necessary for the design of distillation equipment. In general, alkanes show a relatively low reactivity, because their C bonds are relatively stable and cannot be easily broken. Unlike most other organic

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compounds, they possess no functional groups. Oil is a mixture of liquid alkanes and other hydrocarbons. The most important commercial sources for alkanes are natural gas and oil¹. Our current project is devoted to the systematic study of liquid systems containing aliphatic and aromatic hydrocarbons with respect to their environmental importance. From a practical point of view, the data are useful for the design of mixing, storage, and process equipment. This behaviour can be attributed mainly to the specific interactions between unlike molecules of the systems. Our new project is devoted to the systematic study of liquid systems modeling liquid engine fuels.

Nonane and octane are good solvents and non-polar, water in soluble volatile liquids. Nonane and are used as fuels in internal combustion engines, as they vaporize easily on entry into the combustion chamber without forming droplets, which would impair the uniformity of the combustion. The separation of aromatic hydrocarbons (benzene, toluene and xylenes) from aliphatic hydrocarbons (octane and nonane) mixtures is challenging scientists from many years. The aromatic liquids used in this study are very important in petrochemical industries, and several studies on their physical properties at different temperatures and pressures²⁻⁵ have been published.

Xylenes refer to a mixture of three aromatic hydrocarbon isomers, essentially benzene derivatives, which are used as good solvent in the printing, rubber and leather industries. The xylenes are clear, colourless and sweet-smelling liquids that are very flammable. The xylenes are usually refined from crude oil in a process called alkylation. Like other solvents, xylenes are also used as an inhalant drug for its intoxicating properties. In biochemistry, xylene is also used for making slides of specimens hydrophobic in preparation for coverslip mounting. Xylenes are a starting material for the production of other chemicals. For instance chlorination of both methyl groups gives three isomeric xylene dichlorides or 1, 2-bis (chloromethyl) benzenes. With oxidizing agents, such as KMnO_4 , the methyl group can be oxidized to a carboxylic acid. By oxidizing both methyl groups, *o*-xylene forms

phthalic acid. *o*-Xylene is largely used in the production of phthalic anhydride. The major chemical use of metaxylene is in the manufacture of isophthalic acid, which is used as a copolymer to alter the properties of polyethylene terephthalate (PET) making. The PET more suitable for the manufacture of soft drinks bottles.

Vapour-liquid equilibria data are required for design and operation of distillation equipment and for determining the optimal values of parameters in the thermodynamic models. As part of our research program to explore the VLE of various molecular liquids⁶⁻¹¹, we report here the VLE measurements for the binary systems of nonane with octane and octane with orthoxylene and metaxylene at 101.3 kPa with a circulating type apparatus. Our literature survey reveals that there has been no effort to collect the VLE for the mixtures of nonane with octane and octane with orthoxylene and metaxylene. The equations of the NRTL¹² and the UNIQUAC¹³ were used to correlate the experimental VLE data of the binary systems.

EXPERIMENTAL

Materials

In the present study, all the chemicals used were of analytical grade and purchased from commercial sources. The purities of used chemicals were given here in the form of percentage, Nonane (99.98%, Aldrich, USA), octane (99.94%, Aldrich, USA), orthoxylene (99.97%, Alfa Aesar, USA) and metaxylene (99.99%, Acros, USA). The purity of each chemical was checked with gas chromatography failed to show any significant impurities. The purity of the chemicals was assessed by comparing their measured densities (ρ), with Anton Paar (DMA 4500) digital vibrating-tube densimeter, which were in good agreement with the literature values¹⁴⁻¹⁸, as can be seen in Table No.1.

VLE measurements

A recirculation-type phase equilibrium apparatus (NGW Co., Germany) was used in this study to measure the isobaric VLE data. The schematic diagram and the detailed operation procedure have been given by Shiah *et al.*¹⁹. The major parts of the equilibrium apparatus was divided into four major

parts, a liquid-phase chamber, a condenser, a vapor-phase cell and two coil heaters. A silicon oil jacket surrounded the outer spaces of the liquid-phase chamber and the vapor-phase cell. To maintain isothermal condition inside the jacket, the coil heaters were controlled by a PID controller. The top of the equilibrium still was connected to a burette and an adjustable water reservoir to manipulate the total pressure of the system at 101.3 ± 0.2 kPa. The boiling temperature was measured by a series of precision thermometers (models N6000-N6020, stability = 0.1 K, Amarell Electronic Co., Germany). The atmospheric pressure was measured by a Fortin mercury barometer (model 453, stability = 0.1 kPa, Princo Instruments, USA).

The phase compositions were analyzed by gas chromatography (GC) with a thermal conductivity detector. GC model 8700 (China Chromatography, Taiwan) were employed to the isobaric VLE measurements. High-purity Helium (99.99 %) was used as a carrier gas in GC in the present investigation.

The boiling points of mixtures of nonane with hexane, heptane, octane and octane with orthoxylene and metaxylene were measured at 101.3 kPa over the entire range of composition.

RESULTS AND DISCUSSION

In the present study, the isobaric VLE results (T, x and y) were correlated with the γ - ϕ method by using one of the activity coefficient models (the NRTL¹², the UNIQUAC¹³) and assuming that the vapour phase was that of ideal gas mixtures. In the VLE data reduction, the component's fugacity in the vapor phase was calculated from the two-term virial equation of state. The NRTL and the UNIQUAC models were adopted, respectively, to represent the non-ideality of the constituent compounds in the liquid phase. The binary interaction parameters of the solution models (ij value of the NRTL was fixed to be 0.3 through the VLE data reduction) were determined on the basis of the maximum likelihood principle by minimization of the following objective function, Π :

$$\Pi = \sum_{k=1}^{n_p} \left\{ \left[\frac{(P_k^{calc} - P_k^{exp})^2}{\sigma_p} \right] + \left[\frac{(T_k^{calc} - T_k^{exp})^2}{\sigma_T} \right] + \left[\frac{(x_{1,k}^{calc} - x_{1,k}^{exp})^2}{\sigma_{x_1}} \right] + \left[\frac{(y_{1,k}^{calc} - y_{1,k}^{exp})^2}{\sigma_{y_1}} \right] \right\} \quad (1)$$

where T_k^{exp} and T_k^{calc} are the experimental and the calculated boiling point temperatures, respectively, and summation is performed over all experimental points.

The standard deviations of the measured variables are 0.1 kPa for pressure, 0.1 K for temperature, 0.002 for liquid composition, and 0.005 for vapor composition. The Antoine constants for vapour pressures of the pure components were taken from the literature^{14,20,21} and are presented in Table No.2, while the optimized values of the parameters, g12, g21 and of the NRTL, and u12 and u21 of the UNIQUAC are collected in Table No.3. The boiling point temperature versus mole fraction of liquid phase and vapour phase curves are presented in Figure No.1-3. Each binary system has passed the thermodynamic consistency test of Herington²². The smooth curves in the graph are the calculated values from the UNIQUAC model for both the liquid and vapour phases. Such a study on model calculations in addition to presentation of experimental data on binary mixtures are useful to understand the mixing behaviour of liquids in terms of molecular interactions and orientation order-disorder effects. For sake of clarity, we did not show here the other two models, since three models are merging. The close observation of Figure No.1-3 reveals that the curves of three models are overlapping on one another. All these three models with the tabulated parameters represent good agreement with the VLE properties of nonane with octane and octane with orthoxylene and metaxylene at 101.3 kPa. The results reveal that all the systems studied exhibit non-ideal behaviour. In the studied systems especially octane with orthoxylene and metaxylene so the differences in T, x and y can be attributed primarily to the differences in the aliphatic-aromatic interaction energy. For the systems nonane with octane in which the behaviour of vapour and liquid compositions are non ideal. The deviations from ideal behaviour of the systems studied can be

discussed in terms of molecular interactions as follows. On the contrary, in the systems (octane + orthoxylene and metaxylene) we should consider not only the packing effects but also the dominating specific n- interactions. If we observe Figure No.1 closely the gap between liquid phase and vapour phase is wider than that of gap between liquid phase and vapour phase of Figure No.2 and Figure No.3 of nonane with heptane and octane. We can also observe in Figure No.2 the gap between liquid phase and vapour phase is lesser than that of nonane with hexane and wider than that of nonane with octane (Figure No.3). Finally we conclude that the carbon number in alkanes increases non ideal nature decreases. Whereas in the cases of octane with orthoxylene and metaxylene (Figure No.4 and 5) their behaviour is nonideal but tendency is similar because orthoxylene and metaxylenes are isomers. As we shown in Figure No.1-3, nonane with octane and octane with orthoxylene and metaxylene systems show relatively larger deviations from Raoults's law. All systems does not show azeotropic behaviour.

Table No.1: Densities (ρ) at T = 298.15 K and boiling points T of pure components at P =101.3 kPa

S.No	Compound	$\rho /(\text{g}\cdot\text{cm}^{-3})$		T/K	
		This work	Literature	This work	Literature
1	Nonane	0.71374	0.71375 ^a	423.55	424.00 ^d
2	Octane	0.69863	0.69862 ^a	398.33	398.82 ^a
3	Orthoxylene	0.87170	0.87171 ^c	415.98	417.58 ^c
4	Metaxylene	0.86008	0.86009 ^a	412.01	412.25 ^e

^a from reference [14]. ^c from reference [16] ^d from reference [17] ^e from reference [18]

Table No.2: Parameters of the Extended Antoine Equation^a

S.No	Compound	A ^b	B ^b	C ^b	D ^b	E ^b	F ^b	G ^b	T ₁	T ₂
1	Nonane	102.44	-9030.40	0	0	-12.88	7.85E-6	2.00	219.66	594.60
2	Octane	89.17	-7900.20	0	0	-11.00	7.18E-6	2.00	216.38	568.70
3	Orthoxylene	83.49	-7955.00	0	0	-10.08	5.95E-6	2.0	247.98	630.30
4	Metaxylene	81.81	-7741.20	0	0	-9.86	6.07E-6	2.0	286.41	616.20

^a Taken from Aspen property databank

^b Extended Antoine equation: $\ln(P^S) = A - \frac{B}{T} + \frac{C}{T^2} + D_4 T + E_5 \ln T + F_6 T^2 + C_7$ for $T_1 < T < T_2$, where P^S is in kPa and T in K.

$T_1 < T < T_2$, where P^S is in kPa and T in K.

Table No.3: Experimental T , x_1 and y_1 results for the systems of nonane (A) with octane (B) and octane (A) orthoxylene (B) and metaxylene (B) at 101.3 kPa

S.No	T/K	X ₁	Y ₁	T/ K	X ₁	Y ₁
Nonane (A) + Octane (B)						
1	423.54	0	0	406.70	0.6192	0.6982
2	420.72	0.1239	0.1241	404.68	0.7062	0.7694
3	416.18	0.1265	0.1777	402.36	0.8051	0.8562
4	409.92	0.2008	0.2721	399.94	0.9112	0.9381
5	403.49	0.3058	0.3903	398.83	0.9622	0.9796
6	398.64	0.4029	0.4854	398.32	1	1
7	394.55	0.5113	0.5999			
Octane (A) + orthoxylene (B)						
8	398.32	0	0	407.20	0.6358	0.5219
9	398.63	0.0553	0.0440	408.82	0.7175	0.6164
10	399.33	0.1145	0.0969	411.14	0.8311	0.7309
11	400.64	0.2071	0.1751	413.86	0.9183	0.8665
12	402.36	0.3368	0.2642	414.17	0.9271	0.9984
13	403.97	0.4346	0.3532	415.98	1	1
14	405.59	0.5364	0.4431			
Octane (A) + metaxylene (B)						
15	398.32	0	0	412.35	0.6196	0.5348
16	398.63	0.0552	0.0495	404.28	0.7114	0.6335
17	399.13	0.1207	0.1101	405.59	0.8192	0.7578
18	399.94	0.2165	0.1925	407.40	0.8853	0.8853
19	401.05	0.3329	0.2897	409.52	0.9316	0.9991
20	402.16	0.4291	0.3754	410.04	1	1
21	403.27	0.5275	0.4601	411.99		

Table No.4: The NRTL and the UNIQUAC correlated parameters at 101.3 kPa for the systems studied

S.No	System	Model	Parameter/K	Parameter/K	RMSD T^a /K	RMSD P^a /kPa
2	Nonane + octane	NRTL ^{b,c}	g_{12}/R	3466.70	0.63	0.005
			g_{21}/R	403.05		
		UNIQUAC ^b	u_{12}/R	-15000	0.18	0.006
2	Octane + orthoxylene	NRTL ^{b,c}	u_{12}/R	449.62	0.63	0.008
			g_{12}/R	-280.83		
		UNIQUAC ^b	g_{21}/R	-3729.26	0.70	0.007
	u_{12}/R	421.22				
3	Octane + metaxylene	NRTL ^{b,c}	u_{12}/R	-15000	0.58	0.006
			g_{12}/R	-466.69		
		UNIQUAC ^b	u_{12}/R	430.73	0.83	0.005
	u_{12}/R	-15000				

^a $RMSD_{\Delta M} = \sqrt{\frac{1}{np} \sum_{k=1}^{np} (M_k^{calc} - M_k^{exp})^2}$, where n_p is the number of data points and M represents T , P and x_1

^b NRTL model: $T_{ij} = \Delta g_{ij}/RT$; UNIQUAC model: $\ln T_{ij} = \Delta u_{12}/RT$

^cThe value of α was fixed as 0.3 for each binary system

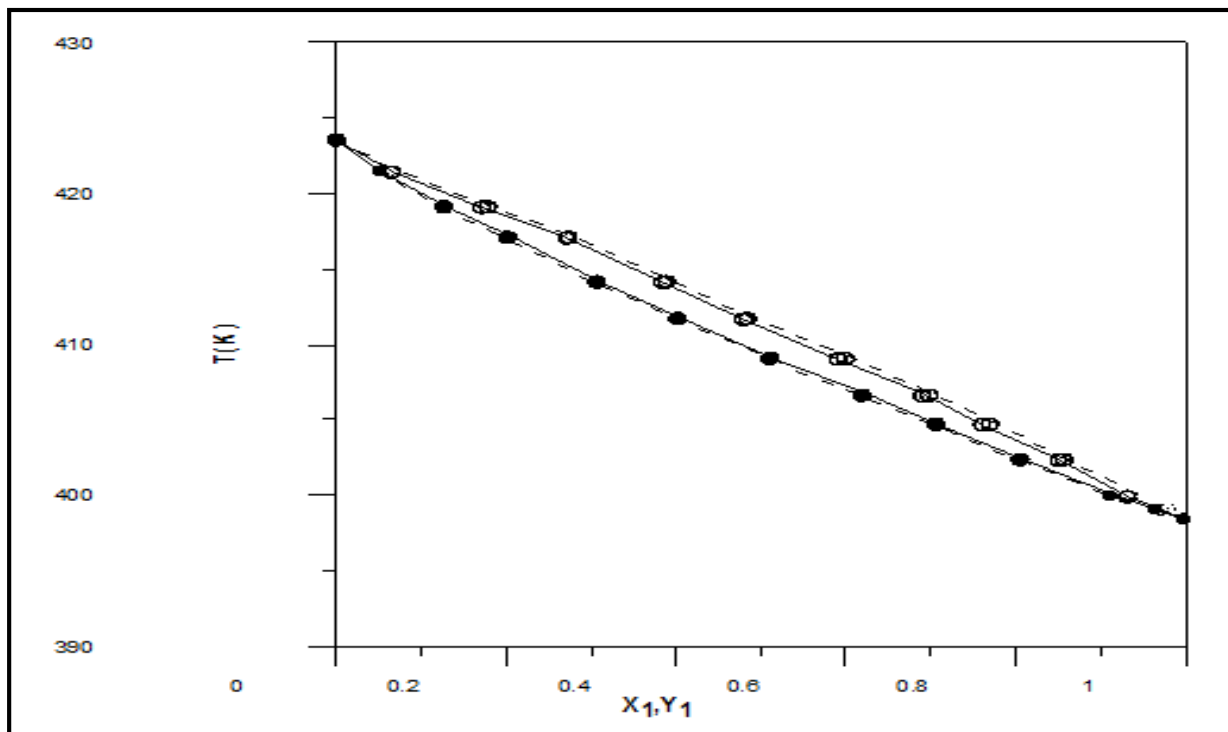


Figure No.1: Plot of experimental boiling point temperatures at 101.3 kPa against mole fraction of nonane (1) and octane (2) (●), —, calculated liquid, vapour composition of the NRTL model, --- calculated liquid, vapour composition of the UNIQUAC model

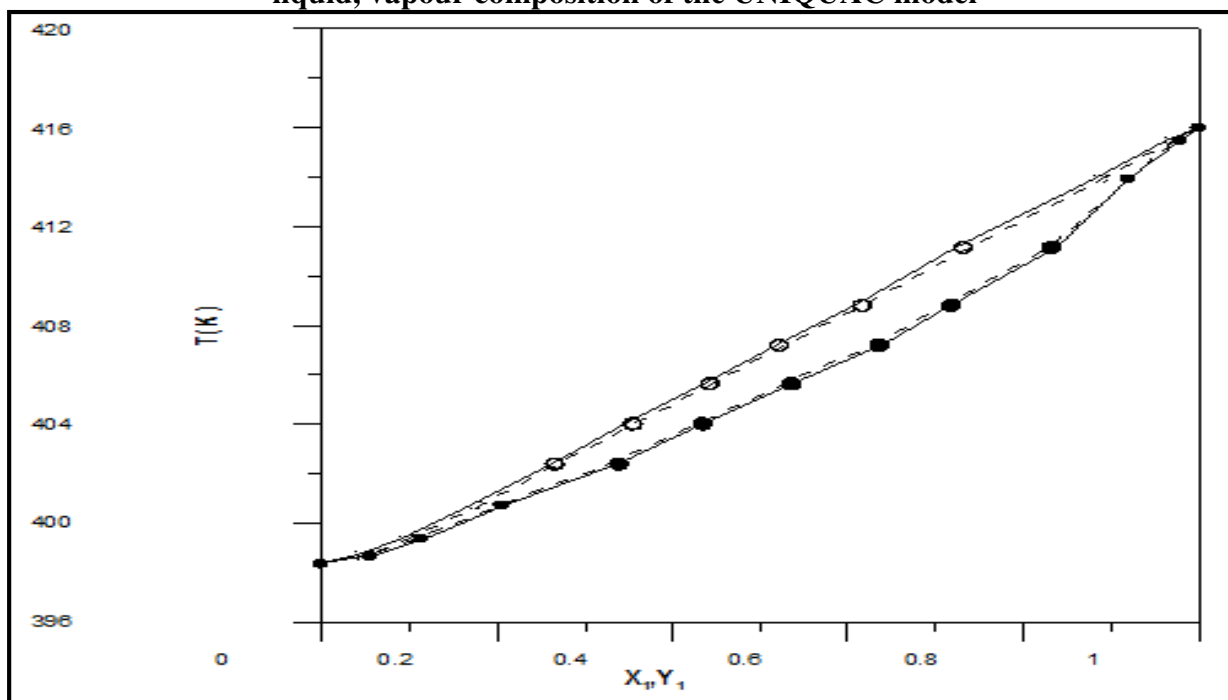


Figure No.2: Plot of experimental boiling point temperatures at 101.3 kPa against mole fraction of octane (1) and orthoxylene (2) (●), —, calculated liquid, vapour composition of the NRTL model, --- calculated liquid, vapour composition of the UNIQUAC model

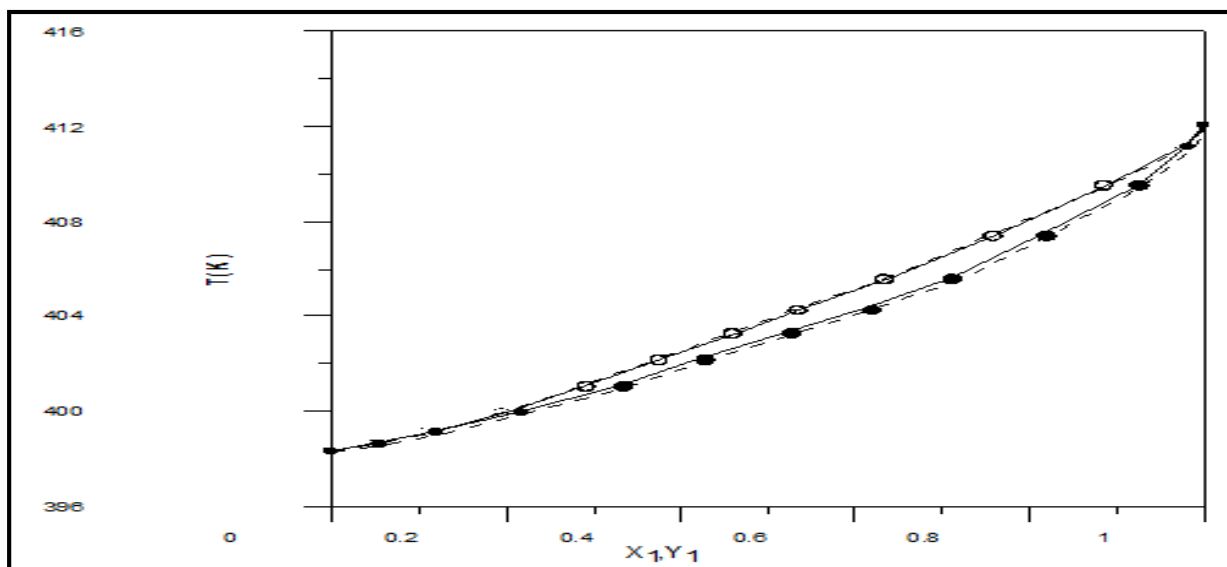


Figure No.3: Plot of experimental boiling point temperatures at 101.3 kPa against mole fraction of octane (1) and metaxylene (2) (●), —, calculated liquid, vapour composition of the NRTL model., --- calculated liquid, vapour composition of the UNIQUAC model

CONCLUSION

Isobaric VLE results have been determined experimentally for binary mixtures composed of nonane with octane and octane with orthoxylene and metaxylene at 101.3 kPa over the entire range of compositions. The NRTL and the UNIQUAC models are capable of accurately correlating the VLE results of the systems investigated. The reported experimental results are satisfactorily correlated with these two models. The results reveal that all the systems studied exhibit non-ideal behaviour.

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CONFLICT OF INTEREST

We declare that we have no conflict of interest.

BIBLIOGRAPHY

1. Morrison R T, Boyd R N. Organic Chemistry, New Jersey: *Prentice Hall*, 6th Edition, 1992, 1360.

- Moravkova L, Wagner Z, Linek J. (p , V_m , T) measurements of (octane + benzene) at temperatures from (298.15 to 328.15) K and at pressures up to 40 MPa, *J. Chem. Thermodyn.*, 40(4), 2008, 607-617.
- Wang Z F, Wang L S, Fan T B. Densities and Viscosities of Ternary Mixtures of Heptane, Octane, Nonane, and Hexyl Benzene from 293.15 K to 313.15 K, *J. Chem. Eng. Data*, 52(5), 2007, 1866-1871.
- Moravkova L, Linek J. Excess molar volumes of (octane + benzene, or toluene, or 1, 3-xylene, or 1, 3, 5-trimethylbenzene) at temperatures between (298.15 and 328.15) K, *J. Chem. Thermodyn.*, 40(4), 2008, 671-676.
- Jasra R V, Nageshkumar V, Ramachandran S, Bhat S G. Excess molar volumes of binary mixtures of alkyl substituted benzene(s) and octane(s) at 298.15K, *Indian J. Technol.*, 26, 1988, 297-300.
- Reddy K D, Rao M V P. Activity coefficients and excess Gibbs free energies for the systems isobutyl methyl ketone (1)-1-pentanol (2) and isobutyl methyl ketone

- (1)-1-hexanol (2), *J. Chem. Eng. Data*, 30(4), 1985, 397-400.
7. Ramadevi R S, Venkatesu P, Rao M V P, Ramakrishna M. Activity coefficients and excess Gibbs free energies for binary mixtures of N, N-dimethylformamide with substituted benzenes, *Thermochim. Acta*, 277, 1996, 133-144.
8. Kumari P G, Rao M V P, Prasad D H L, Kumar Y V L R. Vapor-Liquid Equilibria and Excess Molar Enthalpies for N-Methyl-2-pyrrolidone with Chloroethanes and Chloroethenes, *J. Chem. Eng. Data*, 48(3), 2003, 535-540.
9. Radhamma M, Venkatesu P, Rao M V P, Prasad D H L. Excess enthalpies and (vapour + liquid) equilibrium data for the binary mixtures of dimethylsulphoxide with ketones, *J. Chem. Thermodyn.*, 39(12), 2007, 1661-1666.
10. Radhamma M, Venkatesu P, Hofman T, Rao M V P. Vapor-liquid equilibrium for the binary mixtures of dimethylsulfoxide with substituted benzenes, *Fluid Phase Equilib.*, 262(1), 2007, 32-36.
11. Radhamma M, Hsieh C T, Venkatesu P, Rao M V P, Lee M J, Lin H M. Isobaric Vapor-Liquid Equilibrium for Dimethylsulfoxide with Chloroethanes and Chloroethenes, *J. Chem. Eng. Data*, 53(2), 2008, 374-377.
12. Renon H, Prausnitz Local J M. Compositions in thermodynamic excess functions for liquid mixtures, *AIChE J*, 14(1), 1968, 135-144.
13. Abrams D S, Prausnitz J M. Statistical thermodynamics of liquid mixtures: A new expression for the excess Gibbs energy of partly or completely miscible systems, *AIChE J*, 21(1), 1975, 116-128.
14. Riddick J A, Bunger W B, Sakano T K. Organic Solvents, *Wiley-Inter Science*, New York, 4th Edition, 1986.
15. TRC- Thermodynamic Tables-Hydrocarbons; Thermodynamics Research Center: Texas A and M University System, College Station, TX, extant 1996, fa-1460, 1991, k-1460, 1991.
16. Thermodynamic Tables-Hydrocarbons. Thermodynamics Research Center, The Texas ABM University System: College Station, TX, 1985, a-3290; 1977, d-3291 (loose-leaf data sheets).
17. Weast R C and Grasselli J G. CRC Handbook of Data on Organic Compounds, *CRC Press, Inc., Boca Raton, FL*, 2nd Edition, 1989, 1.
18. Jaime Wisniak, Eti Fishman and Rotem Shaulitch. Isobaric Vapor-Liquid Equilibria in the Systems 2-Butanone + Heptane and 2-Butanone + Oxolane, *J. Chem. Eng. Data*, 43(4), 1998, 537-540.
19. Shiah I M, Yau T S, Tseng H C. Vapor-Liquid Equilibria of Water + Acetic Acid, and Water + Propionic Acid Systems Saturated with Sodium Chloride, *J. Chin. Inst. Chem. Engrs.*, 31(1), 2000, 41-47.
20. Palczewska-Tulinska M, Oracz P. Vapor Pressures of 1-Methyl-2-pyrrolidone, 1-Methyl-azepan-2-one, and 1, 2-Epoxy-3-chloropropane, *J. Chem. Eng. Data*, 52(6), 2007, 2468-2471.
21. Biddiscombe D P, Collerson R R, Handley R, Herington E F G, Martin J F, Sprake C H S. 364. Thermodynamic properties of organic oxygen compounds. Part VIII. Purification and vapour pressures of the propyl and butyl alcohols, *J. Chem. Soc.*, 113, 1963, 1954-1957.
22. Herington E F G. Tests for the consistency of experimental isobaric vapor- liquid equilibrium data, *Institute of Petroleum Journal*, 37, 1951, 457-470.

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