

MEASUREMENT AND MODELLING OF THE EXCESS PROPERTIES OF BINARY AND TERNARY MIXTURES OF CYCLOHEXANE, N- BUTANOL AND 1-OCTANOL AT DIFFERENT TEMPERATURES

www.doi.org/10.62341/mame3276

Mawaheb M. Dardar¹, Mohamed Y. Khalifa², and Mohamed M.
Amer³

1,2,3 Chemical Engineering Department, Faculty of Engineering,
University of Tripoli, Tripoli-Libya
m.dardar@uot.edu.ly

Abstract

This study aims to correlate the excess thermodynamic properties for new desirable mixtures. The density, refractive index, and viscosity of pure components and mixtures were measured over the entire composition range at atmospheric pressure and different temperatures. The results of measuring the density, viscosity, and refractive index were used to calculate the excess molar volumes, viscosity deviation, excess refractive index, and excess activation energies of viscous flow were reported for binary and ternary mixtures of cyclohexane, n-butanol, and 1-octanol at temperatures 20, 30, 40, and 50°C and over the whole mole fraction range. For all of the binary and ternary mixtures the computed excess molar volumes were correlated by applying the Redlich–Kister equation. and Prigogine–Flory–Patterson (PFP) theory. The correlations of excess molar volume, viscosity deviation, excess refractive index and excess activation energy to understand the effect of polar and nonpolar and temperature increase in the systems. Many works carried out to predict the excess thermodynamic properties, but the mixtures of this work have not been studied so far at such conditions. It is hoped that the present work will help in the availability of experimental data for some unknown mixtures to

understand their behavior in the chemical processes, petrochemical industries and design processes.

Keywords: Correlations, Excess properties, Density, Viscosity, cyclohexane and Alcohols, Binary and Ternary mixtures.

قياس ونمذجة الخواص الزائدة للمخاليط الثنائية والثلاثية من سيكلوهكسان و بيوتانول العادي 1- أوكتانول عند درجات حرارة مختلفة

¹مواهب محمد الدررار، ²محمد يخلف خليفة، ³محمد مسعود عامر
قسم الهندسة الكيميائية، كلية الهندسة، جامعة طرابلس، طرابلس، ليبيا

الملخص

تهدف هذه الدراسة إلى ربط الخواص الديناميكية الحرارية الزائدة للمخاليط المرغوبة الجديدة. تم قياس كثافة ولزوجة المكونات والمخاليط النقية على مدى نطاق التركيب الكامل عند الضغط الجوي ودرجات حرارة مختلفة. تم استخدام نتائج قياس الكثافة واللزوجة لحساب الأحجام المولية الزائدة، وانحراف اللزوجة، ومؤشر الانكسار الزائد، وطاقات التنشيط الزائدة للتدفق اللزج للمخاليط الثنائية والثلاثية من سيكلوهكسان، وبيوتانول العادي، 1-أوكتانول عند درجات حرارة 20 و30 و40 و50 درجة مئوية وعلى مدى نطاق الكسر المولي الكامل. بالنسبة لجميع المخاليط الثنائية والثلاثية، تم ربط الأحجام المولية الزائدة المحسوبة من خلال تطبيق معادلة ريدلش-كيسر Redlich-Kister ونظرية بريغوجين-فلوري-باترسون-Prigogine-Flory-Patterson (PFP). الارتباطات بين الحجم الزائد وانحراف اللزوجة ومؤشر الانكسار الزائد وطاقات التنشيط الزائدة لفهم تأثير القطبية وغير القطبية وزيادة درجة الحرارة في الأنظمة. تم إجراء العديد من الأعمال للتنبؤ بالخصائص الحرارية الزائدة، ولكن لم تتم دراسة مخاليط هذا العمل حتى الآن في مثل هذه الظروف. ومن المؤمل أن يساعد العمل الحالي في توفير البيانات التجريبية لبعض المخاليط غير المعروفة لفهم سلوكها في العمليات الكيميائية والصناعات البتروكيمياوية وعمليات التصميم.

الكلمات المفتاحية: الارتباطات، خصائص الفائض، الكثافة، اللزوجة، الهكسان الحلقي والكحولات، المخاليط الثنائية والثلاثية.

Introduction

Extensive studies have been carried out on the thermodynamic properties of binary and ternary mixture systems to understand their thermodynamic behavior. The excess thermodynamic property (M^E) is defined as the disparity between the actual properties (M) and the properties in the ideal case (M^{id}) of a solution at identical temperature, pressure, and composition (Robert, 1987).

In previous papers [Derdar,2015, and Amer 2016], Densities, kinematic viscosities, excess volume, excess viscosities and excess activation energies of viscous flow were reported for binary and ternary mixtures of toluene + n-hexane + n-decane + n-dodecane + hexadecane at temperatures 293.15, 308.15, 323.15 K and over the whole mole fraction range to understand the effect of carbon atom number and temperature increasing in the systems. . In this paper, we extend our studies to the binary and ternary mixtures of cycloalkane (cyclohexane) and alcohols (n-butanol and 1-octanol) at 20, 30, 40, and 50C.

This study aims to provide additional insights into the development of mixed species and their impact on the excess properties of the mixtures. Furthermore, this study will serve as a validation test for various empirical equations designed to correlate property data of binary and ternary mixtures comprising polar and nonpolar components. However, many empirical or semi-empirical equations can be correlated with the density and viscosity data of binary mixtures using several adjustable parameters. The literature on correlations of flow properties for binary and ternary multicomponent liquid mixtures is rather limited. Recently, the empirical and semi-empirical equations for binary mixtures were extended to ternary mixtures by introducing a ternary parameter; also, new models have been developed for the prediction of excess molar volumes, viscosity deviation, excess activation energy, and refractive index of mixtures. Some of them are based on a molecular approach, while others are based on the group contribution concept. The first type of modules require binary interaction parameters for each binary system present in the multicomponent mixture, and

ternary (or higher) constants are generally needed. (Dominguez, et al., 2000).

The possible existence of two or more liquid phases simultaneously must frequently be considered in process applications of phase equilibrium if limited miscibility occurs unexpectedly, it can be a serious disadvantage; for example, two phase pumping and capacity and efficiency are both adversely affected in distillation columns when two liquid phases exit internally. When two liquid phases occur in process flow streams, extra process steps are required to either keep them well mixed if separation is not desired or to allow them to settle when phase separation is desired. If limited liquid phase miscibility is expected, however, advantage can be taken of it in process design liquid-liquid extraction is a powerful separation method based entirely on limited liquid miscibility and the high selectivity of the phases between various components (Arenosa et al., 1972).

In distillation, the overhead product may have limited miscibility after condensation. The liquid phase separation properly considered in design and then gives an additional highly selective stage of separation. If isotropic distillation is used, an additional component not present in the feed stream is added to enhance the relative volatility of the key components. Since this extra component (called the entrained) must subsequently be separated from the product, limited liquid miscibility is highly desirable (Barbe, and Patterson, 1980).

The mathematical treatment of liquid-liquid equilibrium is in many ways more complex than that of vapor-liquid equilibrium. The primary reason for the difficulty is that neither phase is ever an ideal solution. Indeed, if an ideal solution exists in the liquid phase, there can never be more than a single liquid phase formed. The excess volume and viscosity of binary mixtures of cyclohexane and cycloalkanes were discussed in terms of Flory Patterson theory and the absolute rate and free volume theories. The high and negative viscosity deviation ($\Delta\mu$) and excess activation energy of viscous flow (G^{*E}) for large cycloalkanes were attributed to the orientation order in the pure cycloalkanes (Oswal et al., 2005).

Experimental section

2.1 Materials

The anhydrous grade cyclohexane, n-butanol, and 1-octanol were obtained from Sigma-Aldrich. The claimed mole fraction purity for these chemicals was greater than 99%. The purity of all samples was ascertained by comparing the values of their measured densities and viscosities with their literature values at 298.15 K. The determined densities and viscosities of pure components agree well with the literature values given in Table (1), (Liu et al. 2021, Oswala et al. 2005, Hossain et al. 2015, Moosavi et al. 2016, Bhatia et al. 2001)

2.2 Apparatus and Procedure

Calibration of measuring density and kinematic viscosity by using reference compounds. The pure components were degassed ultrasonically and dried over molecular sieves type 4A $1/16$ in. Precautions were taken such as using samples recently prepared and reducing to a minimum the vapor space in the vessels to avoid preferential evaporation during manipulation errors and the subsequent composition errors. The possible error in the mole fraction is less than $\pm 2 \times 10^{-4}$. The densities and viscosities of pure compounds and mixtures were measured by an Anton Paar SVM 3000, and the refractive indices were measured using a refractometer. Water was circulated into the prism of the refractometer by a circulation pump connected to an external thermo-stated water bath.

TABLE 1. Densities, Viscosities, and Refractive Index of the Pure Components at 303.15 K in the Literatures (Liu et al. 2021, Oswala et al. 2005, Hossain et al. 2015, Moosavi et al. 2016, Bhatia et al. 2001), and this work.

Component	ρ (g/cm^3)		ν (cSt)		n_D	
	Literature	This work	Literature	This work	Literature	This work
cyclohexane	0.76912	0.7692	0.821	0.8367	1.4239	1.4173
n-butanol	0.801	0.8008	2.274	2.261	1.3948	1.3905
1-octanol	0.81834	0.8186	6.2071	6.3777	1.4261	1.421

Results and Discussion

The study was done to get the excess thermodynamic properties data experimentally for cyclohexane + n-butanol, cyclohexane + 1-octanol, and n-butanol + 1-octanol in the binary system. In addition, cyclohexane + n-butanol + 1-octanol in ternary system. The study was conducted at five different temperatures 20°C, 30°C, 40°C, and 50°C for the density, viscosity, and refractive index experiments of each mixture.

The experiment results for the binary system are shown in Tables (2, 3, and 4) while, Tables (5, 6, and 7) show the ternary system. The tables displaying the density, viscosity, and refractive index measurements for binary and ternary systems show a clear trend: these properties decrease as the temperature increases.

TABLE 2. Densities for the Binary Systems at Different Temperatures, g/cm³.

Cyclohexane + n-butanol				
Temperatures, C°				
x_i	20	30	40	50
1.00000	0.7787	0.7692	0.7579	0.7502
0.88802	0.7804	0.7717	0.7611	0.7526
0.77898	0.7831	0.7746	0.7645	0.7554
0.67277	0.7863	0.7777	0.7681	0.7587
0.56928	0.7899	0.7812	0.7719	0.7625
0.46840	0.7935	0.785	0.776	0.7666
0.37005	0.7972	0.7891	0.7804	0.7711
0.27412	0.8011	0.7935	0.785	0.7761
0.18052	0.8054	0.7983	0.79	0.7812
0.08917	0.8105	0.8034	0.7952	0.7868
0.00000	0.8167	0.8088	0.8008	0.7926

cyclohexane + 1-octanol				
Temperatures, C°				
x_i	20	30	40	50
1	0.7787	0.7692	0.7579	0.7502
0.933036	0.7824	0.7731	0.7628	0.7546
0.860968	0.7861	0.7772	0.7674	0.759
0.78319	0.7903	0.7817	0.7725	0.764
0.698996	0.7948	0.7863	0.7778	0.7689
0.607558	0.7993	0.7912	0.7831	0.77415
0.507897	0.8041	0.7963	0.7886	0.7797
0.398855	0.8092	0.8016	0.7941	0.78565
0.279038	0.8145	0.8071	0.7998	0.7916

تم استلام الورقة بتاريخ: 2024/6/30م وتم نشرها على الموقع بتاريخ: 2024/7/30م

	0.146769 0	0.81995 0.8256	0.8127 0.8186	0.8057 0.8116	0.79805 0.8045
n-butanol + 1-octanol					
Temperatures, C°					
x_i	20	30	40	50	
1	0.8167	0.8088	0.8008	0.7926	
0.940522	0.8175	0.8097	0.8018	0.7937	
0.875435	0.81835	0.8106	0.8028	0.79481	
0.803908	0.8192	0.81153	0.80385	0.79596	
0.724934	0.8201	0.81247	0.80491	0.79711	
0.637286	0.821	0.81344	0.806	0.7983	
0.539452	0.8219	0.81444	0.80709	0.79951	
0.429548	0.8228	0.81546	0.8082	0.80075	
0.305193	0.82371	0.8165	0.80931	0.802	
0.163335	0.82464	0.81756	0.81044	0.80325	
0	0.8256	0.8186	0.8116	0.8045	

TABLE 3. Viscosity for the Binary Systems at Different Temperatures, mPa s.

cyclohexane + n-butanol					
Temperatures, C°					
x_i	20	30	40	50	
1.00000	0.9747	0.8367	0.7100	0.5828	
0.88802	1.0308	0.8669	0.7412	0.629	
0.77898	1.1501	0.9271	0.7924	0.6782	
0.67277	1.2902	1.031	0.8623	0.719	
0.56928	1.4554	1.1426	0.9532	0.7705	
0.46841	1.6504	1.2812	1.0550	0.8337	
0.37005	1.8684	1.433	1.1680	0.9110	
0.27412	2.1114	1.5957	1.2955	1.0190	
0.18052	2.3649	1.7983	1.4323	1.1432	
0.08917	2.6509	2.0297	1.5898	1.2739	
0.00000	2.9531	2.2610	1.7574	1.4047	

TABLE 3. Continue

cyclohexane + 1-octanol					
Temperatures, C°					
x_i	20	30	40	50	
1.00000	0.9747	0.8367	0.7100	0.5828	
0.933036	1.2925	0.9930	0.96293	0.6783	
0.860968	1.6103	1.1675	0.98901	0.8038	
0.783190	1.9852	1.37925	1.1324	0.916	
0.698996	2.398	1.6910	1.2957	1.0581	
0.607558	2.9438	2.1980	1.58245	1.2719	
0.507897	3.7274	2.7966	1.9692	1.5557	
0.398855	4.7609	3.5840	2.4907	1.91855	
0.279038	5.9944	4.4990	3.2020	2.3514	

تم استلام الورقة بتاريخ: 2024/6/30م وتم نشرها على الموقع بتاريخ: 2024/7/30م

0.146769	7.5249	5.4455	3.9651	2.86375
0.00000	9.0554	6.3777	4.6180	3.4361
n-butanol + 1-octanol				
Temperatures, C°				
x_i	20	30	40	50
1.0000	2.9532	2.261	1.7574	1.4047
0.940522	3.2558	2.4691	1.9148	1.5144
0.875435	3.5977	2.7071	2.0822	1.638
0.803908	3.9699	2.9619	2.2721	1.7776
0.724934	4.3722	3.2467	2.4809	1.9272
0.637286	4.7997	3.5612	2.71035	2.094
0.539452	5.3371	3.9357	2.9758	2.2865
0.429548	6.0400	4.40175	3.30175	2.5125
0.305193	6.9612	4.9778	3.6907	2.7805
0.163335	7.9983	5.6508	4.1309	3.0848
0.0000	9.0554	6.3777	4.6180	3.4361

TABLE 4. Refractive Index for the Binary Systems at Different Temperatures

cyclohexane + n-butanol				
Temperatures, C°				
x_i	20	30	40	50
1.00000	1.423	1.4173	1.412	1.4065
0.88802	1.419	1.4129	1.4071	1.4012
0.77898	1.413	1.4075	1.4019	1.3961
0.67277	1.4075	1.402	1.397	1.392
0.56928	1.4023	1.3971	1.3928	1.3885
0.46841	1.3985	1.3938	1.3898	1.386
0.37005	1.3965	1.3919	1.3881	1.3843
0.27412	1.3958	1.3916	1.3878	1.3838
0.18052	1.396	1.392	1.388	1.3845
0.08917	1.396	1.3919	1.3877	1.3838
0.00000	1.395	1.3905	1.38675	1.383

TABLE 4. Continue

cyclohexane + 1-octanol				
Temperatures, C°				
x_i	20	30	40	50
1.00000	1.423	1.4173	1.412	1.4065
0.933036	1.440	1.4177	1.4131	1.4083
0.860968	1.422	1.4179	1.414	1.41
0.783190	1.4025	1.418	1.4145	1.411
0.698996	1.403	1.4182	1.4148	1.4115
0.607558	1.4233	1.4185	1.415	1.4115
0.507897	1.4665	1.4189	1.4151	1.4115
0.398855	1.5225	1.4194	1.4155	1.4115
0.279038	1.5659	1.420	1.416	1.4119

تم استلام الورقة بتاريخ: 2024/6/30 م وتم نشرها على الموقع بتاريخ: 2024/7/30 م

	0.146769 0.00000	1.55000 1.4254	1.4206 1.421	1.4167 1.4175	1.4127 1.414
n-butanol + 1-octanol					
Temperatures, C°					
x_i	20	30	40	50	
1.0000	1.395	1.3905	1.38675	1.383	
0.940522	1.3979	1.3944	1.3904	1.3866	
0.875435	1.4009	1.3978	1.3938	1.3898	
0.803908	1.40405	1.4007	1.397	1.393	
0.724934	1.4072	1.4035	1.4001	1.3962	
0.637286	1.4104	1.4064	1.4031	1.3995	
0.539452	1.41355	1.4093	1.4061	1.4028	
0.429548	1.41665	1.4124	1.409	1.4061	
0.305193	1.41966	1.4155	1.4118	1.4093	
0.163335	1.4226	1.4184	1.4147	1.412	
0.0000	1.4254	1.421	1.4175	1.414	

TABLE 5. Densities for the Ternary Systems at Different Temperatures.

cyclohexane + n-butanol + 1-octanol					
Temperatures, C°					
x_1	x_2	20	30	40	50
0.07267	0.08247	0.82235	0.8154	0.8082	0.8009
0.04530	0.92544	0.8139	0.8064	0.7984	0.7902
0.90997	0.05737	0.7814	0.7724	0.762	0.7536
0.13694	0.15542	0.81935	0.8124	0.805	0.7976
0.09324	0.84654	0.8116	0.8043	0.7961	0.788
0.81793	0.11603	0.78485	0.7761	0.7665	0.7575
0.12835	0.29132	0.81847	0.8115	0.8038	0.7965
0.26122	0.14823	0.8142	0.8071	0.7996	0.7917
0.18885	0.75015	0.80680	0.79930	0.79090	0.7825
0.74257	0.12039	0.7895	0.7807	0.772	0.7627
0.70595	0.22891	0.78810	0.77930	0.77020	0.7608
0.24554	0.27866	0.81335	0.80620	0.79840	0.7906
0.19800	0.67411	0.80820	0.80050	0.79210	0.7840
0.62751	0.23739	0.79315	0.78430	0.77600	0.7664
0.12077	0.41118	0.81743	0.81030	0.80240	0.7952
0.37451	0.14168	0.80910	0.80160	0.79410	0.7856
0.66132	0.12509	0.79426	0.7857	0.7775	0.7681
0.59698	0.33876	0.79162	0.78270	0.77390	0.7645
0.23163	0.39432	0.81225	0.80480	0.79680	0.7891
0.35296	0.26705	0.8083	0.8006	0.7929	0.7845
0.30101	0.56937	0.8042	0.7961	0.7877	0.7792
0.54303	0.24651	0.7982	0.7896	0.7817	0.7723
0.51565	0.35112	0.7969	0.7880	0.7798	0.7705
0.33376	0.37879	0.80716	0.7991	0.7912	0.7829
0.31654	0.47899	0.80578	0.7976	0.7894	0.781
0.42815	0.36443	0.80205	0.7935	0.7855	0.7766

تم استلام الورقة بتاريخ: 2024/6/30 م وتم نشرها على الموقع بتاريخ: 2024/7/30 م

0.40686	0.46174	0.80057	0.79190	0.78360	0.77470
0.45180	0.25637	0.80330	0.79500	0.78730	0.77840
0.21922	0.49758	0.81098	0.80330	0.79510	0.78740
0.04343	0.11500	0.82330	0.81630	0.80910	0.80190
0.10213	0.04968	0.82146	0.81440	0.80720	0.79990
0.90106	0.07954	0.78100	0.77215	0.76160	0.75320
0.91906	0.03477	0.7818	0.7727	0.7623	0.754
0.02736	0.93141	0.8153	0.80774	0.7997	0.79160
0.20733	0.07843	0.81705	0.81000	0.80266	0.79490
0.06784	0.23099	0.82152	0.81464	0.80718	0.80000
0.83890	0.05950	0.78560	0.77674	0.76720	0.75840
0.13759	0.83279	0.80845	0.80126	0.79300	0.78460
0.04740	0.86074	0.81490	0.80743	0.79940	0.79140

TABLE 6. Viscosity for the Ternary Systems at Different Temperatures.

cyclohexane + n-butanol + 1-octanol					
Temperatures, C°					
x_1	x_2	20	30	40	50
0.07267	0.08247	7.761	5.5406	4.0559	2.9905
0.04530	0.92544	2.9544	2.2418	1.7359	1.3918
0.90997	0.05737	1.1341	0.9064	0.7597	0.6541
0.13694	0.15542	6.4529	4.6606	3.4835	2.5764
0.09324	0.84654	2.948	2.227	1.7065	1.3773
0.81793	0.11603	1.2809	1.0175	0.8569	0.7354
0.12835	0.29132	5.5682	4.0486	3.0657	2.3189
0.26122	0.14823	5.0681	3.7431	2.8294	2.1183
0.18885	0.75015	2.62900	2.00150	1.52630	1.2329
0.74257	0.12039	1.5674	1.2043	0.9872	0.8426
0.70595	0.22891	1.37500	1.11090	0.93820	0.7751
0.24554	0.27866	4.35450	3.24910	2.50050	1.9072
0.19800	0.67411	2.88080	2.18580	1.64140	1.3396
0.62751	0.23739	1.67080	1.33800	1.11720	0.8990
0.12077	0.41118	4.87050	3.57870	2.71820	2.0966
0.37451	0.14168	3.92110	2.95660	2.25260	1.7240
0.66132	0.12509	1.9084	1.4783	1.1766	0.9824
0.59698	0.33876	1.54160	1.23700	1.02650	0.8327
0.23163	0.39432	3.84580	2.88210	2.22340	1.7296
0.35296	0.26705	3.3780	2.5731	2.0318	1.5650
0.30101	0.56937	2.5099	1.9448	1.4908	1.1983
0.54303	0.24651	2.0790	1.6370	1.3569	1.0659
0.51565	0.35112	1.8896	1.5082	1.2405	0.9730
0.33376	0.37879	2.9996	2.312	1.8174	1.4218
0.31654	0.47899	2.7364	2.1168	1.6239	1.2975
0.42815	0.36443	2.3686	1.8572	1.4844	1.173
0.40686	0.46174	2.18900	1.71860	1.35700	1.07720
0.45180	0.25637	2.62770	2.04180	1.64560	1.28390
0.21922	0.49758	3.45640	2.62210	1.98510	1.57170

تم استلام الورقة بتاريخ: 2024/6/30 م وتم نشرها على الموقع بتاريخ: 2024/7/30 م

0.04343	0.11500	7.86180	5.58150	4.09620	3.03430
0.10213	0.04968	7.66390	5.50230	4.00760	2.94510
0.90106	0.07954	1.09640	0.89350	0.75400	0.65150
0.91906	0.03477	1.1957	0.9271	0.7615	0.6648
0.02736	0.93141	3.0887	2.341	1.7987	1.44170
0.20733	0.07843	6.21090	4.54630	3.33630	2.46790
0.06784	0.23099	6.70830	4.84600	3.58580	2.68690
0.83890	0.05950	1.41890	1.07080	0.85560	0.76014
0.13759	0.83279	2.64910	2.01350	1.55890	1.24920
0.04740	0.86074	3.27020	2.46630	1.88510	1.49350

TABLE 7. Refractive Index for the Ternary Systems at Different Temperatures.

cyclohexane + n-butanol + 1-octanol		Temperatures, C°			
x_1	x_2	20	30	40	50
0.07267	0.08247	1.4635	1.419	1.415	1.41
0.04530	0.92544	1.407	1.393	1.389	1.385
0.90997	0.05737	1.4251	1.415	1.41	1.405
0.13694	0.15542	1.4415	1.418	1.414	1.41
0.09324	0.84654	1.407	1.395	1.391	1.387
0.81793	0.11603	1.4235	1.413	1.408	1.403
0.12835	0.29132	1.398	1.415	1.409	1.407
0.26122	0.14823	1.428	1.418	1.413	1.409
0.18885	0.75015	1.41	1.396	1.391	1.387
0.74257	0.12039	1.4195	1.413	1.409	1.405
0.70595	0.22891	1.4235	1.403	1.403	1.398
0.24554	0.27866	1.3932	1.413	1.411	1.407
0.19800	0.67411	1.4185	1.4	1.395	1.391
0.62751	0.23739	1.4215	1.409	1.405	1.401
0.12077	0.41118	1.3985	1.412	1.408	1.405
0.37451	0.14168	1.4105	1.417	1.413	1.409
0.66132	0.12509	1.4105	1.414	1.411	1.406
0.59698	0.33876	1.4221	1.403	1.399	1.393
0.23163	0.39432	1.3951	1.411	1.407	1.404
0.35296	0.26705	1.3928	1.413	1.41	1.407
0.30101	0.56937	1.4224	1.401	1.397	1.393
0.54303	0.24651	1.4122	1.41	1.407	1.403
0.51565	0.35112	1.404	1.405	1.401	1.398
0.33376	0.37879	1.4035	1.409	1.406	1.402
0.31654	0.47899	1.4172	1.405	1.401	1.397
0.42815	0.36443	1.4148	1.407	1.403	1.4
0.40686	0.46174	1.424	1.403	1.398	1.394
0.45180	0.25637	1.4015	1.412	1.408	1.405
0.21922	0.49758	1.4078	1.406	1.404	1.4
0.04343	0.11500	1.4485	1.419	1.415	1.41
0.10213	0.04968	1.4995	1.42	1.416	1.41
0.90106	0.07954	1.4225	1.414	1.408	1.403

0.91906	0.03477	1.4234	1.4164	1.4117	1.406
0.02736	0.93141	1.3994	1.394	1.3898	1.385
0.20733	0.07843	1.4892	1.4194	1.4153	1.41
0.06784	0.23099	1.4231	1.4172	1.4133	1.409
0.83890	0.05950	1.4208	1.4156	1.4114	1.4067
0.13759	0.83279	1.4035	1.3941	1.39	1.3857
0.04740	0.86074	1.4053	1.3972	1.3928	1.3885

The excess molar volume (V^E), viscosity deviations (μ^E), the excess activation energy (G^{*E}), and refractive index (Δn_D) of viscous flow were calculated from the following equations respectively:

$$V_m^E = \frac{\sum_{i=1}^n x_i Mwt}{\rho_m} - \sum_{i=1}^n \frac{x_i Mwt}{\rho_i} \quad (1)$$

$$\mu^E = \mu_m - \sum_{i=1}^n x_i \mu_i \quad (2)$$

$$G^{*E} = RT \left(\ln \mu_m V_m - \sum_{i=1}^n x_i \ln(\mu_i V_i) \right) \quad (3)$$

$$\Delta n_D = n_D - \sum_{i=1}^n x_i n_{Di} \quad (4)$$

Each set of values has been fitted to the Redlich–Kister type equation:

$$M_{ij}^E = x_i x_j \sum_{k=0}^{n_{ij}} a_k (x_i - x_j)^k \quad (5)$$

Where a_i is the polynomial coefficient and k is the polynomial degree. The values of the coefficients a_i are summarized in Table

(8) along with standard deviations $Q^E(x)$ represents, V^E , μ^E , G^{*E} , and Δn_D

The excess properties for the ternary systems have been correlated to Equation (6), the expression proposed by Cibulka [4]:

$$M_{123}^E = \sum_{i<j} x_i x_j \sum_{k=0}^{n_{ij}} a_k (x_i - x_j)^k + x_1 x_2 x_3 (A + B x_1 + C x_2) \quad (6)$$

A , B and C are adjustable parameters, while, $M_{123}^E(x)$ denotes (V^E), (μ^E), (G^{*E}), or Δn_D where M_{ij}^E signifies the three binary contributions assessed by the Redlich–Kister expansion Equation (6). These contributions, represented as M_{ij}^E , are fitted to binary mixture data but computed using ternary mole fractions. This notation is employed to emphasize that $x_i + x_j$ does not equal one. The correlating ability of each of the Equations (5 and 6), was tested by calculating the standard deviations SD between the experimental and the calculated excess properties as

$$SD = \left\{ \frac{1}{n - m} \sum \left[\frac{(M_{exp}^E - M_{cal}^E)}{M_{exp}^E} \right]^2 \right\}^{0.5} \quad (7)$$

The viscosity deviation for the all-binary systems is negative over the entire composition range, and their absolute values decrease as the temperature increases. According to (Fort and Moore, 1969), this behavior is characteristic of systems where dispersive forces predominate. The dominance of the dispersive energy in both the pure components and the mixtures may be inferred from the components of the solubility parameters of (Hansen, 1966)

the (V_{123}^E) values for the ternary system are positive in most of the ternary composition area, but in the region poor in cyclohexane where the values of this property are negative, and show neither maxima nor minima. On the other hand, the values of ($\Delta\mu_{123}$) are negative at all temperatures in all of the composition areas with the

minima localized in the region where the mole fraction of cyclohexane is lower.

The deviation in the refractive indices Δn_D values for cyclohexane +n-butanol mixtures are negative, butanol 1-octanol mixtures are positive and cyclohexane-1-octanol mixtures are positive, this reveals that the strength of specific interaction is not the only factor influencing the viscosity deviation of liquid mixtures. The molecular size and shape of the components also play an equally important role.

It was found that by increasing the carbon chain length of alcohols the excess molar volume shifted to more positive values. Moreover, the obtained positive values of the excess thermal expansion coefficient were in agreement with the variation of excess molar volume against temperature. The excess quantities of molar volume and refractive index were well correlated by the Redlich–Kister equation. The calculated negative values of excess refractive index and viscosity deviation represented no specific interaction between components as shown in Fig. 1. The electronic polarizability of the mixtures increased by increasing n-butanol or 1-octanol concentration because these alcohols are larger and have less electronegative atoms than cyclohexane. The activation energy of flow, determined from viscosity values, decreased with increasing cyclohexane concentration in the binary mixtures. The experimental values of the refractive index and viscosity were well predicted with the Redlich–Kister equation.

TABLE 8. Coefficients a_i of Equation (5) and SDs of Equation (7)

	T, C	a_0	a_1	a_2	SD
Cyclohexane + n-butanol					
$V^E, cm^3/mol$	20	1.8618	-0.20376	1.6431	0.0036
	30	1.7955	-0.04075	-0.00427	0.0029
	40	1.4289	-0.18483	-0.0421	0.0026
	50	2.2716	0.26193	-0.0483	0.0052
$\Delta\mu, mPa \cdot s$	20	-1.79176	2.43626	-5.25922	0.00342
	30	-1.26392	0.07652	-0.15909	0.00633
	40	-0.85325	0.02608	-0.08327	0.00152
	50	-0.73384	0.25027	0.25886	0.00476
$G^{*E}, J/mol$	20	-878.767	1,105.1	411.935	58.06
	30	-1,060.93	-0.0120	-193.706	55.82
	40	-886.076	-592.756	-295.588	3.73

تم استلام الورقة بتاريخ: 2024/6/30 م وتم نشرها على الموقع بتاريخ: 2024/7/30 م

	50	-1,089.01	0.0244	957.645	21.22
n^E	20	-0.00092	-0.15022	0.01289	0.00071
	30	-0.03693	0.00399	0.03853	0.00021
	40	-0.03500	0.00013	0.02774	0.00018
	50	-0.03271	-0.00470	0.01902	0.00029
cyclohexane + 1-octanol					
$V^E, cm^3/mol$	20	1.36543	-0.25848	0.03922	0.00921
	30	1.24790	-0.16961	0.09161	0.00501
	40	0.50001	-0.02496	-0.00645	0.01315
	50	1.49047	-0.40755	-0.11005	0.01289
$\Delta\mu, mPa s$	20	-4.88507	-0.92150	2.90411	0.01572
	30	-3.02385	-2.24554	1.47348	0.02385
	40	-2.70839	-1.09559	2.88277	0.03439
	50	-1.73199	-0.33545	0.70883	0.01030
$G^{*E}, J/mol$	20	6251.32	-28318.77	51105.67	44.79
	30	2019.72	-1579.16	-267.72	37.15
	40	746.88	-997.54	3481.60	126.09
	50	890.07	-639.16	1849.12	46.32
n^E	20	0.66569	-3.35828	5.70914	0.06290
	30	-0.00100	-0.00088	0.00375	0.00005
	40	0.00173	0.00671	0.00662	0.00004
	50	0.00511	0.01549	0.00794	0.00010

	T, C	a_0	a_1	a_2	SD
n-butanol + 1-octanol					
$V^E, cm^3/mol$	20	0.07223	-0.00837	0.06249	0.00109
	30	0.12968	-0.03471	-0.04050	0.00080
	40	0.09674	-0.01948	0.03056	0.00110
	50	0.12143	-0.01237	-0.04143	0.00071
$\Delta\mu, mPa s$	20	-1.63026	-0.45582	1.90710	0.01947
	30	-0.86032	-0.16156	0.72924	0.00677
	40	-0.37109	-0.10607	0.35980	0.00375
	50	-0.20709	-0.02448	0.11642	0.00236
$G^{*E}, J/mol$	20	1232.851	1498.076	-14145.722	8.13
	30	765.518	144.978	499.309	3.47
	40	842.136	174.375	371.268	3.16
	50	787.954	190.383	191.334	2.90
Δn_D	20	0.01930	-0.00953	0.01906	0.00021
	30	0.01850	0.00720	0.01149	0.00016
	40	0.02004	0.00846	0.00471	0.00005
	50	0.02199	0.00186	0.00551	0.00010

TABLE 9. Coefficients A , B , and C of Equation (5) and SDs of Equation (6)

	T, C	A	B	C	SD
cyclohexane + n-butanol + 1-octanol					
$V^E, cm^3/mol$	20	-9.53580	1.51818	8.99679	0.0152
	30	-17.85161	15.76768	19.21911	0.0150
	40	-11.06529	-2.76940	18.55873	0.0067
	50	-21.85849	18.31382	21.56748	0.0203
$\Delta\mu, mPa \cdot s$	20	-15.05197	-7.15678	42.34081	0.13870
	30	-7.94072	6.82887	8.71559	0.02783
	40	1.91622	-2.39768	-4.48253	0.03264
	50	1.25516	-1.41521	-2.90795	0.00667
$G^{*E}, J/mol$	20	-47052.0	51038.3	-9500.6	941.3
	30	162845.8	-164193.9	-320925.6	835.0
	40	166432.6	-160582.0	-328806.4	804.8
	50	156149.1	-149958.4	-307764.9	768.1
Δn_D	20	-30.35378	33.98438	41.52628	0.11042
	30	0.04402	0.09172	0.08096	0.00073
	40	0.05731	0.03622	0.04358	0.00064
	50	0.00499	0.10241	0.10736	0.00099

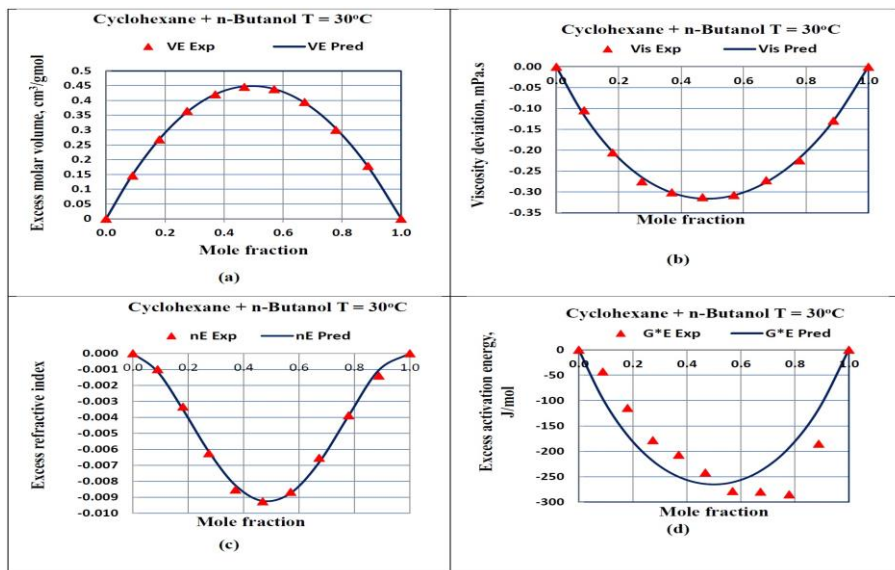


Figure. 1: Comparison between experimental data and prediction values for excess molar volume, viscosity deviation, excess refractive index, and excess activation energy at 30°C.

Conclusion

The excess properties were determined by measuring the experimental densities, viscosities and refractive indices of cyclohexane + n-butanol + 1-octanol at the temperature range of 20° to 50°C over the whole composition range and atmospheric pressure. The excess molar volume, obtained from density, was positive for both the studied binaries and the ternary increased with temperature rising. The positive excess molar volume is ascribed to the weak interactions between unlike molecules. The calculated negative values of excess refractive index and viscosity deviation represented no specific interaction between components. The results indicate that for cyclohexane and alcohol mixtures the Redlich–Kister equation predicts the experimental data well, showing smallest deviations. The fitting of this equation for excess activation energy in producing the experimental gives the largest deviations.

Nomenclature

M^E	= Molar excess property
M	= Molar property
V	= Molar volume
G	= Molar Gibbs free energy
V^E	= Molar excess volume
μ^E	= Excess viscosity
G^{*E}	= Molar excess activation energy
n^E	= Excess refractive index
x_i	= Mole fraction of pure compound i
R	= Universal gas constant
μ_m & μ_i	= Viscosity of mixture and pure component i
ρ_m & ρ_i	respectively
V_i	= Density of mixture and pure component i
Mwt	respectively
	= the volume of pure component i
	= Molecular weight of the pure compound

References

- Alonsu M. C., J. L. P. Vilches, R. G. Sanchez-Pajares and J. N. Delgado, (1983), “J. Chem. Thermodynamics”, 15(10), pp: 913-917.
- Amer M. M, M. M. Dardar, A. A. Arajeji, and K. M. Mezughi, (2016), University Bulletin Issue No. 18 – Vol. (1), pp:18-37.
- Arenosa R. L., C. Henduina, G. Taradajos and M. Dias Pena, (1972), “J. Chem. Thermodynamics”, 11(1), pp:825-832.
- Bhatia A. C., N. Tripathi, and G.P. Dubey (2001) Indian J pure & appl phys, vol. 39, pp: 776-780.
- Barbe M., and D. Patterson, (1980), “J. Solution Chem”, 9(10), pp: 753-769.
- Delmas G., P. Purves, and P. De Saint-Romain, (1975), “J. Phy. Chem.”, 79(18), pp:1970-1974.
- Deepika and S. Pandey, (2023), “Liquids”, 3, pp:48–56
- Dardar M. M., and M. M. Amer, (2015), Al-Ostath Issue 8.
- Dikko A. B. and A. Alkasim (2012), “International J of Recent Research in Physics and Chemical Sciences”, 1(2), pp:8-12.
- Dikko A. B., A. D.Ahmed,T. Pascal, and A. Alkasim (2014) “International J of Recent Research in Physics and Chemical Sciences”, 3(9), pp:306-308.
- Dominguez M., J. L. Pardo, I. Gascon, F. Roya, and J.Urieta (2000),“Fluid phase Equilibria”, 169(2), pp:277-292.
- Finkers H. J.m J. C. Bosma, and A.A. Broekhuis, (2011) “Chemical Engineering Science” 66, pp:2889-2897.
- Fort R.J. and W.R. Moore, (1966), Trans. of Faraday Society, vol. 62, pp: 1112-1119.
- Hossain M.N., M. M. Rocky, and S. Akhtar (2015), “Journal of Chemical & Engineering Data”.
- Hansen C.M., (1969), “Industrial & Engineering Chemistry Product Research and Development”, vol.8, pp:2-11.
- Kumar A., O. Prakash, and S. Prakash, (1981), “J. Chem. Eng. Data”, 26(1), pp:64-67.

- Jayalakshmi T., and K. S. Reddy, (1985), “J. Chem. Eng. Data”, 30(1),pp: 51-53.
- Morrison R. T., and N. Boyd, (1973), “Organic Chemistey” Allyn and Bacon, INC. 3rd edition, New York University.
- Moosavi M., A. Motahari, A. Vahid, V. Akbar, A. Rostami, and A. Omrani, (2016), Journal of Chemical & Engineering Data.
- Patil P.P., S. R. Patil, A. U. Borse, and D. G. Hundiwale, (2011), “Rasayan J. Chem.”, 4(3), pp:599-604.
- Pang F., C. Seng, T. Teng, and M.H. Ibrahim, (2007), “Journal of Molecular Liquids”, 136, pp:71-78.
- Padmanaban R., Ahobilam G., Aanantha I. G., Dong-Eun Lee and Kannan V., “Comparative Evaluation of Viscosity, Density and Ultrasonic Velocity Using Deviation Modelling for Ethyl-Alcohol Based Binary Mixtures”, Appl. Sci. 2023, 13, 7475, 1-14.
- Liu X., S. Xue , R. Ikram , C. Zhu , Y. Shi , and M He, (2021), J. the science and technology of fuel and energy, 268, pp:1-11.
- Oswala S.L., K.D. Prajapatib , P. Oswalc , N.Y. Ghaela , S.P. Ijardara, (2005), Journal of Molecular Liquids 116, pp: 73 – 82
- Robert A. Alberty, (1987),“physical Chemistry” 7th edition.
- Reddy D. R., and M. V. Prabhakara Rao, (1985), “J. Chem. Eng. Data”, 30(1), pp:38- 42.
- Sameti M. R., and M. Rakhshi, (2011), “African Journal of pure and Applied Chemistry”, 5(7), pp:158-167.
- Smith J., H. C. Van Ness, and M. M. Abbott (2022), “Introduction to Chemical Engineering Thermodynamics” 7th edition, Mc Graw Hill.
- Vadamalar R., P. Mani, R. Balakrishnan, and V. Arumugam, (2009), “E-Journal of Chemistry”, 6(1), pp:261-269.
- Visak Z. P., A. G. Ferreira, and I. M Fonseca, (2000), “J. Chem. Data”, 45, pp:926-931.
- Wu J., A. Nhaesi, A. Fattah, and A. Asfour (1999), “Fluid phase Equilibria” 164(2), pp: 285-293.

Yingmin Yu L. Z.,* Zhaohui Liao, Xiaosheng Xu, Xin Huang, Bing Jia, and Qingsong Li (2020), "Liquid-Liquid Equilibrium for the Ternary Systems Water + 1-Butanol + 1-Hexanol or 1-Octanol at 303.15, 313.15, and 323.15 K" J. Chem. Eng. Data, 65, 477-486.