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DENSITY AND VISCOSITY MEASUREMENTS OF AQUEOUS SOLUTIONS OF 2−METHOXYETHANOL AT TEMPERATURES (298.15, 303.15, 308.15, AND 313.15) K

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Abstract

Densities and viscosities have been measured for the binary mixtures of 2–methoxyethanol (2–ME) and water at 298.15, 303.15, 308.15 and 313.15 K. From the precise density measurements, the excess molar volume (V^E) were calculated, V^E results are negative over the entire range of mole fractions and become less negative as the temperature increases. The deviation in viscosity ($\Delta\eta$) and excess molar Gibbs free energy of activation of viscous flow (ΔG^{*E}) have been calculated from experimental viscosity measurements at different temperatures. $\eta\Delta$ and ΔG^{*E} data are positive over the whole mole fraction range.

The observed results of V^E, $\eta\Delta$ and ΔG^{*E} are discussed in terms of molecular interactions in these binary mixtures. Generally, molecular interactions dominant these behaviors are of type, disruption and formation of intra–and interhydrogen bonding between like and unlike molecules, respectively and dipole–dipole interaction. The experimental excess functions V^E, $\eta\Delta$ and ΔG^{*E} were fitted to the Redlich–Kister polynomial equation to evaluate the adjustable parameters and standard deviation from ideality.

Introduction

2-Methoxyethanol is the first member of alkoxyalkanols and used extensively as solvent and solublizing agent in many industries with interests ranging from pharmaceutical to plastic products. From theoretical point of view, it is very interesting molecule having the ability to form intra–and intermolecular hydrogen bonds. On the other hand, alkanols (alcohols) are the most well– known solvents with protic and self –associated properties.

2 Methoxyethanol, an ether alkanol, shows physiochemical characteristic midway between protic and dipolar aprotic solvents(1).

Studies on excess functions of binary liquid mixtures are of considerable importance in understanding the nature of molecular interactions that determined by intermolecular forces (hydrogen bonding, charge transfer complex, Van der Waals forces, etc.) (2,3). To determine the extent and type of interactions between 2–ME and water molecules, the densities and viscosities of binary mixtures of 2-ME with water have been measured.

Experimental

2–Methoxyethanol ($CH_3OCH_2CH_2OH$) was obtained from Aldrich Chemical Company, with purity > 99 %. The solvent was kept on activated molecular sieves type 4 A^o for 24 hours then filtered before use. Bidistilled deionized water, its conductivity (0.6×10^{-6} $s.cm^{-1}$) was used. The experimental measured values of density, ρ and viscosity η for both solvents are agreed well with those values published in the literature (4-8), Table (1).

Table (1)
Comparison of Densities, ρ, and Viscosities, η, of Pure Components with Literature Data at 298.15 K.

Component	ρ/ g.cm^{-3}		η/ cp	
	Obs.	Lit.	Obs.	Lit.
2–Methoxyethanol	0.96029	0.96010$^{(4)}$ 0.96041$^{(8)}$ 0.96002$^{(7)}$ 0.96015$^{(6)}$	1.523	1.507 $^{(6)}$ 1.541$^{(7)}$
Water	0.99705	0.96015$^{(6)}$ 0.99731$^{(7)}$ 0.99705$^{(5)}$	0.888	0.891$^{(6)}$

All mixtures were prepared by using determined volumes to obtain samples covering the whole range of mole fraction ($0 > x > 1$). Mixtures were kept in air tight stoppered bottle to revent any contamination. The possible error in mole fraction is estimated to be less than $\pm 1\times10^{-4}$.

Densities of pure liquids and their mixtures were determined using a digital densimeter (Anton paar DMA 60/ 602), the density values were reproducible to within 1×10^{-5} g.cm^{-3}. On the other hand, the viscosity of pure liquids and binary liquid mixtures were measured using a Schot–Gerate (AVS 300) viscometer thermostated with a digital water bath (T 1500). The flow times were determined electronically with an electric timer of precision ±0.01 s. The accuracy in the measurements of viscosity was ± 0.001 mPa.s.

Results and Discussion

The experimental results for the density (ρ) of the aqueous solution of 2– ME at 298.15, 303.15, 308.15 and 313.15 K are listed in Table (2). The excess molar volume, V^E, was calculated from the following equation $^{(9)}$:

$$V_m^E/(\mathrm{cm^3mol^{-1}}) = \frac{X_1M_1+X_2M_2}{\rho}{}_2 - X_1\frac{M_1}{\rho_1} - X_2\frac{M_2}{\rho_2} \ldots\ldots(1)$$

where x_1, x_2, M_1, M_2, ρ_1 and ρ_2 represent the mole fraction, molecular weight and the density of the pure component liquids 1 and 2 respectively. ρ is the density of the mixture. Excess molar volumes calculated from eq.1 are listed in Table (2).

The experimental results for the viscosity (η) are presented in Table 3. Fig. (2) showed the variation of viscosity as a function of the mole fraction of 2–ME, this figure show maxima at about 0. 30 mole fraction of 2– ME.

The viscosity deviations, ηΔ are obtained by:

$$\Delta\eta/\mathrm{cp} = \eta_{12} - x_1\eta_1 - x_2\eta_2 \,\ldots\ldots\ldots (3)$$

where η_{12} is the viscosity of the mixture and x_1, η_1 and x_2, η_2 are the mole fraction and viscosity of pure components 1 and 2, respectively. The viscosity deviation, Δη, at 298.15, 303.15, 308.15 and 313.15 K are presented in Table (3). ηΔ is plotted as a function of 2– ME mole fraction, Fig. (3). ηΔ values are positive as the temperature increases with maxima at about 0.35 mole fraction of 2– ME.

Table (2)
Densities ρ, and Excess Molar Volumes, V^E for binary mixtures of x_1 2– ME + x_2 water at different temperatures.

X_1	T=298.15 K		T=303.15 K	
	ρ/g.cm^{-3}	V^E/cm^3.mol^{-1}	ρ/g.cm^{-3}	V^E/cm^3.mol^{-1}
0.00000	0.99705	0.0000	0.99565	0.0000
0.02562	1.00005	-0.1336	0.99762	-0.1204
0.09221	1.00602	-0.4784	1.00237	-0.4514
0.19159	1.00722	-0.8521	1.00267	-0.8163
0.35615	0.99679	-1.0308	0.99181	-0.9879
0.68084	0.97522	-0.6967	0.97046	-0.6801
1.00000	0.96029	0.0000	0.95558	0.0000
X_1	**T=308.15 K**		**T=313.15 K**	
	ρ/g.cm^{-3}	V^E/cm^3.mol^{-1}	ρ/g.cm^{-3}	V^E/cm^3.mol^{-1}
0.00000	0.99403	0.0000	0.99222	0.0000
0.02562	0.99543	-0.1156	0.99377	-0.1242
0.09221	0.99993	-0.4784	0.99699	-0.4495
0.19159	0.99884	-0.8006	0.99541	-0.7946
0.35615	0.98737	-0.9663	0.98337	-0.9548
0.68084	0.96595	-0.6735	0.96162	-0.6608
1.00000	0.95098	0.0000	0.94669	0.0000

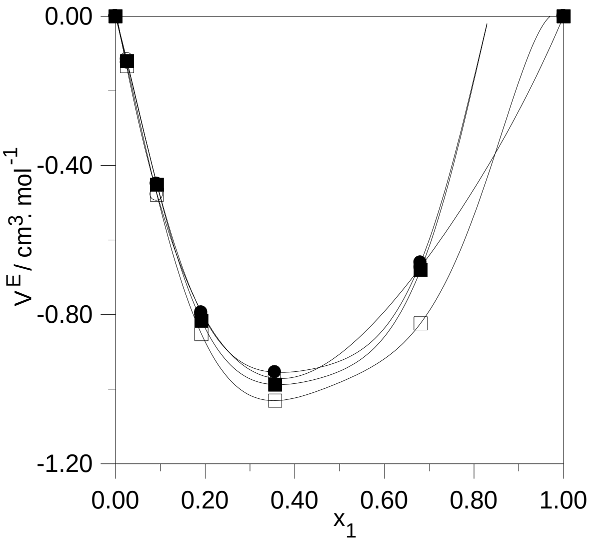

Fig. (1) : Excess molar volumes, V^E, for (x_1 2– ME + x_2 water) versus x_1 at different temperatures: (□) 298.15; (■) 303.15; (○) 308.15; (●) 313.15 K.

Table (3)

Viscosities η, Viscosity deviations, ηΔ, and Excess Molar Gibbs free energy of activation of viscous flow, ΔG^{*E} for binary mixtures of x_1 2– ME + x_2 water at different temperatures.

X_1	**T=298.15 K**			**T=303.15 K**		
	η/cp	**Δη /cp**	**ΔG^{*E}/ kJ.mol^{-1}**	**η/cp**	**Δη /cp**	**ΔG^{*E}/ kJ.mol^{-1}**
0.00000	0.888	0.000	0.0000	0.793	0.000	0.0000
0.02562	1.161	0.257	0.7256	1.019	0.211	0.6958
0.09221	1.931	0.985	2.0873	1.655	0.809	2.0212
0.19159	2.679	1.670	2.9459	2.289	1.385	2.9353
0.35615	2.865	1.751	3.0182	2.453	1.454	2.9623
0.68084	2.142	0.822	1.7115	1.885	0.698	1.6937
1.00000	1.523	0.000	0.0000	1.372	0.000	0.0000

X_1	**T=308.15 K**			**T=313.15 K**		
	η/cp	**Δη /cp**	**ΔG^{*E}/ kJ.mol^{-1}**	**η/cp**	**Δη /cp**	**ΔG^{*E}/ kJ.mol^{-1}**
0.00000	0.714	0.000	0.0000	0.647	0.000	0.0000
0.02562	0.907	0.179	0.6786	0.811	0.152	0.6539
0.09221	1.438	0.676	1.9632	1.258	0.567	1.9049
0.19159	1.969	1.154	2.8187	1.699	0.961	2.7388
0.35615	2.123	1.222	2.9110	1.848	1.031	2.8558
0.68084	1.663	0.591	1.6734	1.481	0.508	1.6468
1.00000	1.241	0.000	0.0000	1.127	0.000	0.0000

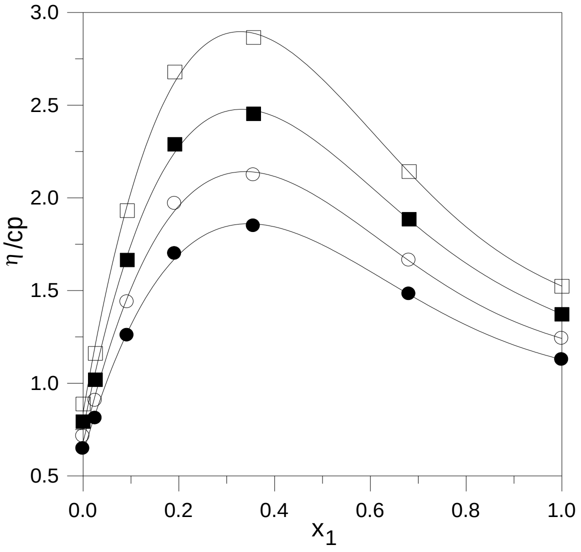

Fig.(2) : Viscosity, η, of ($x_1$2 – ME + x_2 water) versus x_1 at different temperatures: (□) 298.15; (■) 303.15 (○); 308.15; (●) 313.15 K..

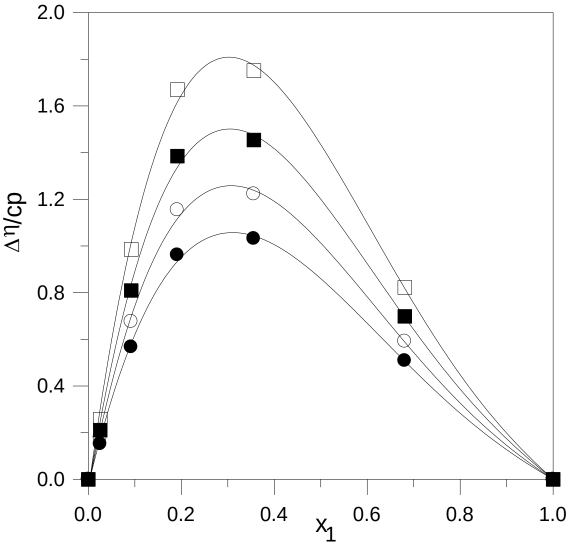

Fig. (3) : Excess Viscosity, Δη, of ($x_1$2– ME + x_2 water) versus x_1 at different temperatures: (□) 298.15; (■) 303.15; (○) 308.15; (●) 313.15 K.

The excess molar Gibbs free energy of activation of viscous flow, ΔG^{*E}, have been calculated from density and viscosity data according to the equation [(10)]:

$$\Delta G^{*E} = RT\left[\ln \eta_m V_m - x_1 \ln \eta_1 V_1 - x_2 \ln \eta_2 V_2\right] \qquad \text{.................................} (4)$$

where x_1 and x_2 are the mole fraction of 2–ME and water respectively. η_m, η_1 and η_2 are the viscosity of mixture, 2–ME and water respectively. V_m, V_1, and V_2 are the molar volume of mixture, 2–ME and water respectively. The calculated ΔG^{*E} values are given in Table (3). For the mixture studied, the ΔG^{*E} values are positive over the whole mole fraction range at all temperatures as shown in Fig.(4).

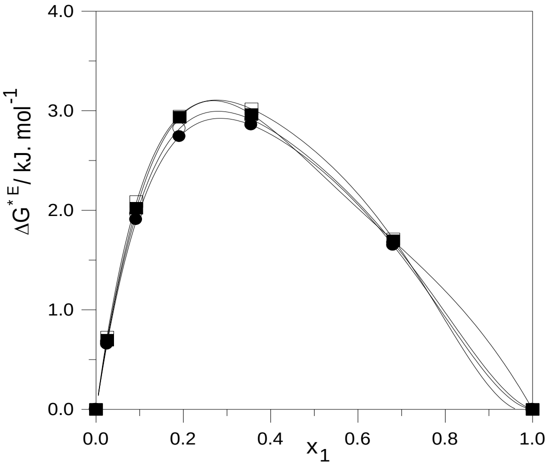

Fig. (4) : Excess activation energy of viscous flow, ΔG^{*E}, of ($x_1$2– ME + x_2 water) versus x_1 at different temperatures: (□) 298.15; (■) 303.15; (○) 308.15; (●) 313.15 K.

The calculated values of V^E, $\eta\Delta$ and ΔG^{*E} were fitted to a Redlich – Kister polynomial equation [(11)]:

$$Y^E = x_1 x_2 \sum_{j=0}^{n} A_j (x_2 - x_1)^j \qquad \text{.......}\ \ldots(5)$$

where Y^E the excess property, V^E, $\eta\Delta$ or ΔG^{*E} and n is the number of adjustable parameters A_j in each case for all mixtures, the optimum number of adjustable parameters is ascertained from an examination of the variation in standard deviation, σ, as given by[(12)]

$$\sigma(Y^E) = \left[\frac{Y^E_{obs} - Y^E_{cal}}{N - P}\right]^{1/2} \qquad \text{.................} (6)$$

where N represent the number of experimental points and P the number of adjustable parameters. The values of these parameters, A_j, along with the standard deviation, σ are listed in Table (4).

Table (4)
Redlich – Kister coefficients A_j and Standard deviation, σ for the excess molar quantities of solution of (x_1 2– ME + x_2 water) at different temperatures.

Property	T/K	A_o	A_1	A_2	σ
V^E/cm^3.mol^{-1}	298.15	-3.9048	2.0963	-0.3944	0.0184
	303.15	-3.7721	1.9492	-0.3438	0.0215
	308.15	-3.6774	1.8637	-0.5687	0.0206
	313.15	-3.6167	1.8822	-0.6085	0.0178
Δη /cp	298.15	5.8038	-6.2956	1.7829	0.0545
	303.15	4.8437	-5.1442	1.4975	0.0471
	308.15	4.0754	-4.2854	1.2228	0.0367
	313.15	3.4527	-3.5371	1.0069	0.0275
ΔG^{*E}/ kJ.mol^{-1}	298.15	9.5797	-8.8119	11.4716	0.0389
	303.15	9.4436	-8.6695	11.2966	0.0126
	308.15	9.3228	-8.3462	10.5877	0.0285
	313.15	9.1843	-8.1216	10.0275	0.0299

Excess molar volumes (V^E) are negative over the entire range of mole fractions and become less negative as the temperatures increases Fig.(1). Fig.(1) shows that the minimum lies at a mole fraction of about 0.35 2–ME. Many effects may contribute to the negative value of V^E. These effects are the disruption of (i) intramolecular hydrogen bonding of 2–ME and H_2O themselves (ii) intramolecular dipolar interaction in 2– methoxyethanol (iii) the possible formation of hydrogen – bond interactions between 2–ME and H_2O and (iv) the interstitial accommodation of the component into the other. Many studies in the literature (13-15) on water and 2–ME mixture agree with our present results are indicated that intramolecular hydrogen bonding exists in 2–ME in the liquid state. Moreover, the values of the Kirkwood correlation factor, g_k (give an idea about the intermolecular forces between the solution contents through the dielectric constant measurements)(16,17), for pure 2–ME in the temperature range 25, 35, and 45 ^oC are not much greater than unity (the g_k of 2–ME are 1.483, 1.478, and 1.463, respectively). These values indicated that 2–ME is relatively, unstructured liquid having strong but not specific dipole – dipole interaction.

Fig.(2) shows that the $\Delta\eta$ values of mixtures of 2–ME and water are positive over the whole mole fraction range at all temperatures passes through a maxima at a mole fraction of 0.35 2–ME which also gives an indication of the presence of specific interaction between 2–ME and water molecules, supports the V^E behavior(18,19). On the other hand, the ΔG^{*E} values was also positive, the positive deviation from ideality of $\Delta\eta$ and ΔG^{*E} for mixture were attributed to the larger and positive interaction effect of 2–ME and H_2O that also supports the results obtained for V^E.

References

[1] T.L.Ionic,. "Densities and Refractive Indices of the Binary Mixtures Containing Methanol, Ethanol, 1,2-Ethanediol, and 2-Methoxyethanol at 298.15 K. " J.Chem.Soc.Faraday Trans., Vol.89, No.1,1993, pp.733-740.

[2] A.Marchetti and L.Tassi, "Denities and Excess Molar Volumes of the Solvent (Ethane-1,2-diol + 2-Methoxyethanol + Water) from T = 263.15K to T= 353.15K", J. Chem. Thermodyn. Vol.30, No 5, 1998, pp.653-669.

[3] C. Coquelet, A. Valtz, X. Courtial, D. Richon, "Excess Molar Volumes of Binary Mixtures of N, N-Dimethylformamide with Water at Temperatures from 277.13 to 318.15 K", Thermochim. Acta, Vol.448, No.2, 2006, pp. 47–51.

[4] L.Albuquerque, C.Ventura and R.Goncalves, "Densities and Volumetric Properties of 2-Methoxyethanol with N,N-Dimethylformamide and Water at Different Temperatures", J. Mol. Liq. Vol. 123, No. 30, 2006, pp. 130-135.

[5] M.A.Rubio, J.A.Gonzalez, and J.C.Cobos, "Physiochemical Properties of a Binary Mixtures of Water + 1,2-Ethanediol, +2-Methoxyethanol,+2-Ethoxyethanol, and 2-butoxyethanol at 308.15 K", J.Chem. Eng. Data, Vol. 43, No. 2, 2000, pp.811-818.

[6] T.M.Aminabbavi, and B.Gopalakrishna, "Density, Viscoity, and Refractive Index of Binary Mixtures of Water with N,N-Dimethylformamide, Dimethylsulfoxide, 2-Methoxyethanol at 298.15 K", J. Chem. Eng. Data, Vol.40, No.2, 2002, pp.856- 862.

[7] B.Das and D.Hazra, "Excess Molar Volumes of Binary Mixtures of 2-Methoxyethanol + Water at Different Temperatures",J. Chem. Eng. Data, Vol.38, No.3 2003, pp.361-368.

[8] M. N. Roy, B. Sinha, and V. K. Dakua, "Liquid-Liquid Equilibria Data for 2-Methoxyethanol or 2-Ethoxyethanol + Dodecane",J. Mol. Liq. Vol.136, No.1, 2007,pp.128-134.

[9] E.Jimenez, C. Franjo, and M. I. PazAndrade, "Densities and Excess Molar Volumes of Binary Mixtures Containing Isobutyl alcohol, Ethanol, and 2-Methylpentene at 298.15 K", J. Chem. Eng. Data, Vol.42, No.2, 1997, pp. 262-268.

[10] G.Delmas, P.Parves, P. dest Romian, "Densities and Viscosities of Binary Mixtures of N-Formylmorpholine and an

Aromatic Hydrocarbon", J.Phys. Chem., Vol.79, No. 1, 1998, pp. 197-202.

[11] O.Redlich and A. T. Kister, "Algebric Representation of Thermodynamic Properties and the Classification of Solutions", Ind. Eng. Chem., Vol.40, No.3 1948, pp.345-347.

[12] F. Kohler, "Physical and Thermodynamic Properties of Pure Chemicals", Data Compilation,Monatsh. Chem., Vol.91, No.2, 1960, pp.738-742.

[13] G.Douheret and A. J. Pal, "Excess Molar Volumes, Excess Viscosities, and Excess Activation Energies of Viscous flow for 2-Methoxyethanol + Water and + Sulfolane at 303.15 K", J. Chem. Eng. Data, Vol.17, No.1, 1988, pp.601-605.

[14] G.Roux, G. Perron, and J. E. Desnoyers, "AThermodynamic Investigation of Aqueous 2-Methoxyethanol",J. Chem. Thermodyn., Vol.25, No.1, 1993, pp. 139-154.

[15] G.Douheret, A. Pal, and M.I.Davis, "Viscometric and Volumetric Behavior of Binary Mixtures of 2-Methoxyethanol + Water at Different Temperatures". J.Chem. Thermodyn., Vol.22, No. 1, 1990, pp. 99-105.

[16] H. Frohlich, "Theory of Dielectric", 2 nd ed, Claredon press, 1958, Oxford, U. K. pp. 20-40.

[17] J. G. Kirkwood, "Dielectric Constant, Intermolecular Forces, and Optical Rotation of Organic Compounds", "J. Phys. Chem. ", Vol.84, No.3, 1966, pp.695-698.

[18] M. Mazrul, M. Monirul, and M. N. Yeasmin, "Viscosity of Aqueous Solutions of 2-Methoxyethanol, 2-Ethoxyethanol. and Ethanolamine", J.Chem. Thermdyn. Vol. 36, No. 10, 2004, pp. 889-893.

[19] M.Cocchi, and A.Marchetti, "Kinematic Viscosities of Binary Mixtures Containing 2-Methoxyethanol and water from -10 ^{o}C to 80 ^{o}C, " Fluid Phase Equilibria, Vol. 157, No. 2, 1999, pp. 317-342.

الخلاصة

تم في هذا البحث قياس الكثافة و اللزوجة لمحاليل 2- ميثوكسي ايثانول + الماء لاربعة درجات حرارية 298.15 ، 303.15 ، 308.15 و 313.15 كلفن و على مدى الكسر المولي. تم حساب الحجوم المولارية الفائضة V^E من القيم العملية للكثافات و لقد وجد ان هذه القيم تنحرف سلبا عن السلوك المثالي على المدى الكامل من الكسر المولي و يزداد النحراف السالب كلما زادت درجات الحرارة. باستخدام قيم اللزوجة العملية تم حساب انحراف اللزوجة عن المثالية $\eta\Delta$ و كذلك طاقة كبس الحرة الفائضة ΔG^{*E} للمحاليل و على مدى الكسور المولية و درجات الحرارة المختلفة و لقد وجد ان قيم $\eta\Delta$ و ΔG^{*E} تنحرف ايجابا عن المثالية و يزداد هذا الشذوذ كلما زادت درجة الحرارة.

تم مناقشة نتائج V^E، $\eta\Delta$ و ΔG^{*E} بالاعتماد على نوع التأثيرات المتبادلة الحاصلة بين 2- ميثوكسي و الماء و التي تم تشخيصها على انها قد تكون تكسر و تكون الاواصر الهيدروجينية الضمنية و البينية بين الجزيئات المتشابهة و المختلفة على التوالي او من نوع تأثر ثنائي القطب – ثنائي القطب. تم تعيير القيم العملية لجميع الدوال الفائضة V^E، $\eta\Delta$ و ΔG^{*E} باستخدام معادلة ردلخ – كستر متعددة الحدود و تم ايجاد الحدود المتعددة للمعادلة و استخدام النتائج لحساب الانحراف القياسي عن المثالية لهذه القيم.