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Index

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Research Paper Physics

Refractive Indices, Densities And Excess Properties For Liquid Mixtures (Cetane + Alkanols) At Different Temperatures

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ABSTRACT

Refractive index and density have been measured at (293,298,303) K for binary mixtures of Cetane + 1-Alkanols (C_4-C_6) over the whole mole fraction range. From these data the excess molar volume, excess molar refraction and excess refractive index were calculated. These quantities are discussed in terms of intermolecular interactions as well as role of hydrogen bonding upon refractive indices of liquid mixtures.

Keywords : Refractive index, density, excess parameters, intermolecular, Interactions

Introduction

The excess values of molar volume, molar refraction is quite useful in understanding the solute-solvent interactions in the liquid mixtures. The non-zero value of these parameters gives deep insight into the molecular interactions, arrangements and structural behavior. we present here the experimental results of the refractive index, n_m , and the density, ρ , for the binary mixtures of Cetane(C) with 1-Butanol(B), 1-Pentanol(P), 1-Hexanol(H) at (293,298,303)K over the whole mole fraction range. From these results, the excess molar volume (V^E), excess molar refraction (R^E) and excess refractive index (Δn_m) have been calculated over the whole mole fraction range, from which valuable information about intermolecular interactions between the components can be deduced.

Experimental Section

The refractive index of mixtures was measured using Abbe refractometer. Before measuring refractive index on Abbe refractometer inspection of scale was made using test piece. The refractometer was calibrated with distilled water before each use. The temperature was maintained constant with the help of thermostatically controlled water bath (accuracy ±0.01K).Our refractive indices are accurate up to ±.0001. The sample mixtures were directly injected into prism assembly of the instrument with the help of a plastic syringe The densities were measured with a bicapillary pycnometer having a bulb volume of about 10 cm^3 and an internal diameter of about 1mm. The pycnometer was calibrated at (293,298,303) K with doubly distilled water. The pycnometer was immersed in water bath whose temperature was maintained constant by circulating the coolant liquid.

Theory

The various physical parameters were calculated from the measured values of refractive index (n_m) and density (ρ) using the following formulae:

$$V^E = \left(\frac{X_1M_1 + X_2M_2}{\rho}\right) - \left(\frac{X_1M_1}{\rho_1} + \frac{X_2M_2}{\rho_2}\right) \quad (1)$$

$$R^E = \frac{(n_m^2-1)}{(n_m^2+2)}\left(\frac{X_1M_1+X_2M_2}{\rho}\right) - \left[\frac{(n_1^2-1)}{(n_1^2+2)}\frac{M_1}{\rho_1}\phi_1 + \frac{(n_2^2-1)}{(n_2^2+2)}\frac{M_2}{\rho_2}\phi_2\right] \quad (2)$$

$$\Delta n_m = n_m - (x_1 n_1 + x_2 n_2)$$

Where X1 and X_2 are mole fractions of respective components; ρ, ρ_1, and ρ_2 are the densities and n_m n_1 and n_2 are the measured refractive indices of the mixture and the pure component liquids, respectively. M_1, M_2 are the molecular weights and ϕ_1, ϕ_2 are volume fractions of respective components in liquid mixtures.

Results

Experimentally find out densities (), refractive indices (n_m) and calculated values of V^E, R^E and Δn_m for mixtures (C+B), (C+P), (C+H) are given in Table 1 to 3 respectively. Values of V^E and R^E for mixtures (C+B), (C+P), (C+H) at T=293 K are plotted with respect to mole fraction of Cetane(X_1) and shown in Fig. 1 and 3, respectively. The variation of V^E and R^E with mole fraction of Cetane(X_1) for system (C+B) for all the three temperatures viz. 293K, 298K, 303K are shown graphically in Fig. 2 and 4 respectively.

Discussion

Excess parameter provides information about intermolecular interactions to the great extent the negative values of V^E indicates the presence of strong intermolecular interactions in the system. From figure (1) it is observed that V^E, for all systems have negative values over the entire range of mixture composition. Negative values of excess molar volume point to a closer packing of molecules because in the present case there is large difference between molar volumes of Cetane and 1-Alkanols as molar volume, at temp 293K, are 292.9874 cm^3 mol^{-1} and 91.0680 cm^3 mol^{-1}, for Cetane and 1-Butanol, respectively.

Hydrogen bonds plays a role in reducing the experimental values of refractive index in alcohol containing systems, which may also results in negative value of deviations. The observed negative deviation of V^E confirms the presence of strong molecular association in the system. Hence it is concluded that there exists strong inter molecular interactions in system. The negative values of V^E follow the sequence (C+B) > (C+P) >(C+H). However except of (C+B) system the negative values of V^E for other system are very close to each other. The effect of temperature on excess molar volume for (C+B) system is shown in figure (2).

Excess molar refraction represents the complex electronic perturbation between liquid components due to orbital mixing of components. R^E gives the strength of interaction in a mixture and is sensitive function of mixture composition. From figure (3) it is observed that R^E have very large negative values for all systems over the entire range of mixture composition. This further supports the existence of strong interaction in these systems. The order of negative magnitude of R^E values is same as existed for V^E i.e. (C+B) > (C+P) >(C+H). This again supports the existence of strong interaction between unlike molecules of mixtures. The highest value of R^E for (C+B) mixture suggests that interaction between Cetane and 1-Butanol is strongest as compared to that between Cetane and other 1-Alkanols. Figure (4) represents the effect of temperature on R^E for system (C+B). It is observed that as temperature increases almost no effect in the negative value of R^E is obtained, for all the systems under consideration.

Conclusions

Thus from above mentioned discussion, it may concluded that the variation of excess parameters with concentration and temperature strongly supports the molecular association in these liquid mixtures. The effects observed for all the systems under investigation show dependence on hydrogen bonding of components of mixture. It may also conclude that refractometric study of liquid mixtures provides a better insight for a comprehensive investigation of molecular association between molecules of mixtures.

Figure1 V^E as a function of mole fraction of Cetane (X1) for mixture (C+ B), (C+ P), (C+ H) at T= 293K

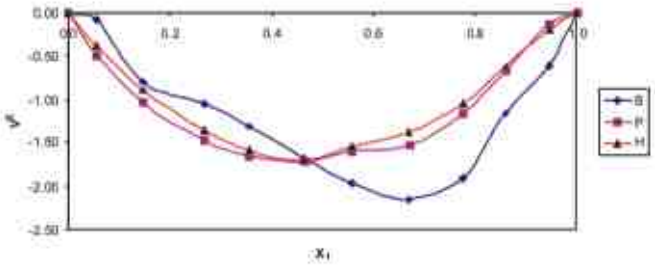

Figure2 V^E as a function of mole fraction of Cetane (X_1)formixture(C+B)attemperature293K,298K,303K

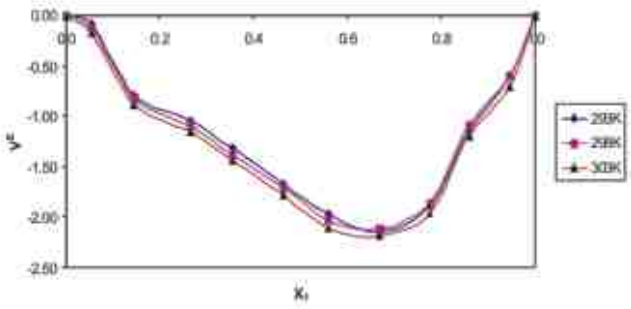

Figure3 R^E as a function of mole fraction of Cetane (X_1) for mixture (C+ B), (C+ P), (C+ H) at T= 293K

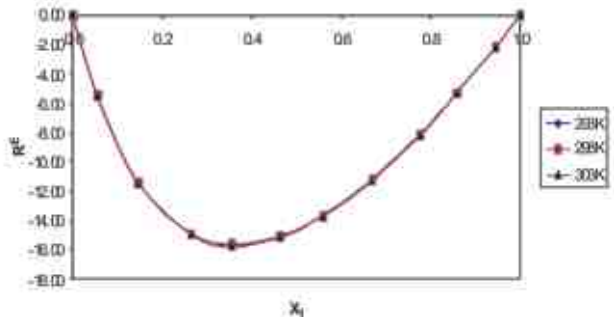

Table 1 Refractive index (n_m),density (ρ), excess molar volume (V^E), excess molar refraction (R^E), excess refractive index (Δn_m) for mixture Cetane and 1-Butanol at 293K, 298K, 303K as a function of the mole fraction X_1 of Cetane

T	X_1	ρ (g cm^{-3})	n_m	V^E (cm^3 mol^{-1})	R^E (cm^3 mol^{-1})	Δn_m
293K	0.0000	0.8091	1.3985	0.0000	0.0000	0.0000
	0.0540	0.8041	1.4039	-0.0801	-5.4591	0.0035
	0.1460	0.8015	1.4111	-0.7911	-11.4295	0.0074
	0.2650	0.7955	1.4175	-1.0509	-14.9210	0.0096
	0.3550	0.7924	1.4212	-1.3121	-15.6427	0.0101
	0.4630	0.7897	1.4245	-1.6701	-15.1080	0.0095
	0.5580	0.7877	1.4270	-1.9602	-13.6948	0.0086
	0.6690	0.7852	1.4293	-2.1532	-11.2264	0.0070
	0.7750	0.7819	1.4311	-1.9021	-8.1731	0.0050
	0.8590	0.7780	1.4324	-1.1593	-5.2806	0.0033
	0.9450	0.7752	1.4335	-0.6121	-2.1615	0.0014
	1.0000	0.7729	1.4341	0.0000	0.0000	0.0000
298K	0.0000	0.8017	1.3978	0.0000	0.0000	0.0000
	0.0540	0.7977	1.4032	-0.1253	-5.4372	0.0035
	0.1460	0.7957	1.4102	-0.8234	-11.3905	0.0072
	0.2650	0.7904	1.4168	-1.0902	-14.8616	0.0096
	0.3550	0.7878	1.4203	-1.3852	-15.6086	0.0099
	0.4630	0.7853	1.4237	-1.7155	-15.0637	0.0095
	0.5580	0.7837	1.4261	-2.0332	-13.6778	0.0085
	0.6690	0.7811	1.4285	-2.1276	-11.1821	0.0070
	0.7750	0.7780	1.4302	-1.8674	-8.1471	0.0050
	0.8590	0.7743	1.4315	-1.0947	-5.2637	0.0033
	0.9450	0.7719	1.4324	-0.6137	-2.2048	0.0011
	1.0000	0.7695	1.4332	0.0000	0.0000	0.0000
303K	0.0000	0.7995	1.3971	0.0000	0.0000	0.0000
	0.0540	0.7956	1.4024	-0.1772	-5.4901	0.0034
	0.1460	0.7932	1.4094	-0.8803	-11.4763	0.0072
	0.2650	0.7875	1.4158	-1.1573	-14.9728	0.0094
	0.3550	0.7847	1.4194	-1.4464	-15.7102	0.0099
	0.4630	0.7820	1.4227	-1.7806	-15.1645	0.0094
	0.5580	0.7803	1.4251	-2.1267	-13.7687	0.0085
	0.6690	0.7775	1.4274	-2.1963	-11.2620	0.0069
	0.7750	0.7744	1.4291	-1.9685	-8.2163	0.0049
	0.8590	0.7706	1.4304	-1.2077	-5.3135	0.0032
	0.9450	0.7680	1.4315	-0.7123	-2.1944	0.0013
	1.0000	0.7655	1.4321	0.0000	0.0000	0.0000

Table 2 : Refractive index (n_m), density (ρ), excess molar volume (V^E), excess molar refraction (R^E),excess refractive index (Δn_m) for mixture Cetane and 1a-Pentanol at 293K, 298K, 303K as a function of the mole fraction X_1 of Cetane

T	X_1	ρ (g cm^{-3})	n_m	V^E (cm^3 mol^{-1})	R^E (cm^3 mol^{-1})	Δn_m
293K	0.0000	0.8139	1.4100	0.0000	0.0000	0.0000
	0.0683	0.8103	1.4140	-0.4862	-4.9253	0.0024
	0.1693	0.8053	1.4186	-1.0338	-9.4630	0.0045
	0.2483	0.8022	1.4213	-1.4722	-11.4385	0.0053
	0.3648	0.7964	1.4246	-1.6443	-12.4742	0.0058
	0.4519	0.7927	1.4266	-1.713	-12.2438	0.0057
	0.5739	0.7875	1.4289	-1.5839	-10.8299	0.0051
	0.6508	0.7850	1.4301	-1.5332	-9.4863	0.0044
	0.7492	0.7811	1.4314	-1.1664	-7.2658	0.0033
	0.8734	0.7769	1.4329	-0.667	-3.9155	0.0019
	0.9622	0.7738	1.4338	-0.1332	-1.1851	0.0006
	1.0000	0.7729	1.4341	0.0000	0.0000	0.0000
298K	0.0000	0.8103	1.4081	0.0000	0.0000	0.0000
	0.0683	0.8070	1.4122	-0.5096	-4.9582	0.0024
	0.1693	0.8022	1.4170	-1.1110	-9.5219	0.0047
	0.2483	0.7991	1.4199	-1.5601	-11.4998	0.0056
	0.3648	0.7931	1.4233	-1.7042	-12.5331	0.0060
	0.4519	0.7895	1.4254	-1.7875	-12.3064	0.0060
	0.5739	0.7845	1.4278	-1.7139	-10.9012	0.0053
	0.6508	0.7818	1.4290	-1.6306	-9.5449	0.0046
	0.7492	0.7779	1.4304	-1.2454	-7.3111	0.0035
	0.8734	0.7738	1.4319	-0.7691	-3.9658	0.0019
	0.9622	0.7706	1.4328	-0.1857	-1.2221	0.0005
	1.0000	0.7695	1.4332	0.0000	0.0000	0.0000
303K	0.0000	0.8067	1.4069	0.0000	0.0000	0.0000
	0.0683	0.8037	1.4111	-0.5740	-4.9904	0.0025
	0.1693	0.7990	1.4158	-1.2313	-9.5930	0.0046
	0.2483	0.7957	1.4188	-1.6481	-11.5677	0.0056
	0.3648	0.7898	1.4222	-1.8405	-12.6169	0.0061
	0.4519	0.7858	1.4243	-1.8616	-12.3695	0.0060
	0.5739	0.7812	1.4266	-1.8863	-11.0016	0.0052
	0.6508	0.7783	1.4279	-1.7622	-9.6179	0.0046
	0.7492	0.7741	1.4293	-1.3068	-7.3546	0.0035
	0.8734	0.7700	1.4308	-0.8525	-3.9988	0.0019
	0.9622	0.7667	1.4317	-0.2404	-1.2364	0.0006
	1.0000	0.7655	1.4321	0.0000	0.0000	0.0000

Table 3 Refractive index (n_m),density (ρ), excess molar volume (V^E), excess molar refraction (R^E), excess refractive index (Δn_m) for mixture cetane and 1-Hexanol at 293K, 298K, 303K as a function of the mole fraction X_1 of Cetane

T	X_1	ρ (g cm^{-3})	n_m	V^E (cm^3 mol^{-1})	R^E (cm^3 mol^{-1})	Δn_m
293K	0.0000	0.8133	1.4175	0.0000	0.0000	0.0000
	0.0711	0.8095	1.4200	-0.3894	-3.6910	0.0013
	0.1735	0.8046	1.4229	-0.8896	-7.1602	0.0025
	0.2592	0.8016	1.4249	-1.3523	-8.8471	0.0031
	0.3430	0.7980	1.4266	-1.5836	-9.6112	0.0034
	0.4467	0.7936	1.4283	-1.6892	-9.6604	0.0034
	0.5741	0.7881	1.4301	-1.546	-8.6407	0.0031
	0.6507	0.7851	1.4310	-1.3811	-7.6038	0.0027
	0.7493	0.7812	1.4320	-1.0461	-5.8663	0.0021
	0.8527	0.7775	1.4330	-0.6223	-3.6560	0.0013
	0.9311	0.7747	1.4336	-0.1858	-1.7553	0.0006
	1.0000	0.7729	1.4341	0.0000	0.0000	0.0000
298K	0.0000	0.8095	1.4163	0.0000	0.0000	0.0000
	0.0711	0.8059	1.4189	-0.4268	-3.7025	0.0014
	0.1735	0.8012	1.4218	-0.9357	-7.1920	0.0026
	0.2592	0.7982	1.4239	-1.4171	-8.8770	0.0032
	0.3430	0.7949	1.4256	-1.6940	-9.6623	0.0035
	0.4467	0.7907	1.4273	-1.8617	-9.7282	0.0035
	0.5741	0.7850	1.4291	-1.6480	-8.6970	0.0031
	0.6507	0.7817	1.4300	-1.4261	-7.6364	0.0027
	0.7493	0.7778	1.4311	-1.0745	-5.8822	0.0021
	0.8527	0.7741	1.4320	-0.6570	-3.6801	0.0013
	0.9311	0.7714	1.4327	-0.2594	-1.7695	0.0007
	1.0000	0.7695	1.4332	0.0000	0.0000	0.0000
303K	0.0000	0.8057	1.4149	0.0000	0.0000	0.0000
	0.0711	0.8022	1.4175	-0.4547	-3.7293	0.0014
	0.1735	0.7975	1.4205	-0.9720	-7.2341	0.0026
	0.2592	0.7944	1.4227	-1.4631	-8.9178	0.0033
	0.3430	0.7910	1.4243	-1.7314	-9.7142	0.0035
	0.4467	0.7868	1.4261	-1.8980	-9.7749	0.0035
	0.5741	0.7811	1.4279	-1.6859	-8.7440	0.0031
	0.6507	0.7778	1.4289	-1.4632	-7.6693	0.0028
	0.7493	0.7740	1.4299	-1.1397	-5.9319	0.0021
	0.8527	0.7703	1.4309	-0.7042	-3.7107	0.0013
	0.9311	0.7676	1.4316	-0.3153	-1.7946	0.0007
	1.0000	0.7655	1.4321	0.0000	0.0000	0.0000

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