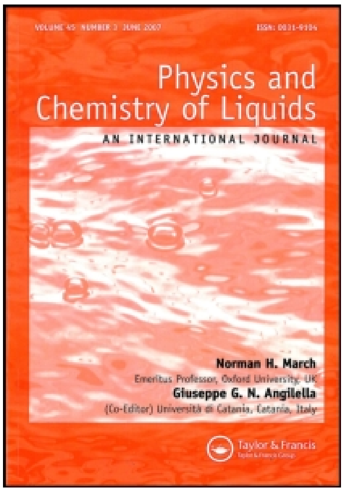

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Evaluation of Excess Molar Volumes of n -butanol with nitrobenzene-aniline-acetonitrile Binary Liquid Mixtures at Temperatures of 298.15, 303.15, 308.15, and 313.15 K

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EVALUATION OF EXCESS MOLAR VOLUMES OF *n*-BUTANOL WITH NITROBENZENE–ANILINE–ACETONITRILE BINARY LIQUID MIXTURES AT TEMPERATURES OF 298.15, 303.15, 308.15, AND 313.15 K

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The excess molar volumes (V_m^E) of binary liquid mixture defined here: *n*-butanol and nitrobenzene, *n*-butanol and aniline, and *n*-butanol and acetonitrile have been determined as a function of mole fraction of *n*-butanol at temperatures of 298.15, 303.15, 308.15, and 313.15 K by a calibrated bi-capillary pycnometer. The V_m^E were obtained as negative values over the entire composition range in the order of *n*-butanol + nitrobenzene, < *n*-butanol + aniline, and < *n*-butanol + acetonitrile systems. The negative magnitude of V_m^E suggests the presence of specific intermolecular interaction in the three liquid mixtures.

Keywords: Excess molar volumes; Binary liquid mixtures; *n*-butanol; Nitrobenzene; Aniline; Acetonitrile

INTRODUCTION

Over the past three decades, various efforts have been made in understanding the theoretical and practical importance of binary/ternary liquid mixtures [1–6]. The physicochemical analysis has been found to be a useful tool for getting sound information about the structure and interactions of various liquid–liquid binary/ternary mixtures. The physicochemical properties of binary/ternary liquid mixtures such as alcohols and hydrocarbons have drawn a considerable interest in experimental and theoretical aspects [7–9]. Physical properties including dipole moment, thermodynamic properties have been reported in the literatures [10,11]. Besides the theoretical importance, the knowledge of physicochemical properties of multi-component mixtures is indispensable for chemical process industries. Examples are the petroleum or petrochemical industry

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where physicochemical processes are involved to handle the mixtures of hydrocarbons such as alcohols, aldehydes, ketones etc. Importantly, it is necessary to know the interaction between the components of mixtures for accurate designing of equipment.

To investigate the property of binary liquid mixtures, a framework was developed in our laboratory and some studies have been reported [12–16]. The present article describes the excess molar volumes of (x) *n*-butanol $+ (1-x_1)$ nitrobenzene, or $x + (1-x_1)$ aniline, or $x + (1-x_1)$ acetonitrile in obtaining the information of interaction of the liquid mixtures at temperatures of 298.15, 303.15, 308.15, and 313.15 K. This is a continuation of a previous investigation [16].

EXPERIMENTAL

Materials and Procedure

The compounds *n*-butanol (purity 99.5%, Merck), acetonitrile (purity 99%, Fluka), nitrobenzene (purity 99.5% Merck), and aniline (analytical grade, Metheson, USA, purity 99.5%), were used. The density of the pure components and binary mixtures was measured by calibrated bi-capillary pycnometer and the density measurement method was reported elsewhere [14,16]. Special attention was given to avoid the evaporation of solutions after preparation. The purity of the chemical was compared with the literature values [17–20] (Table I) and the obtained values showed a good agreement with reported values [11,16,19,20].

The V_m^E of different binary mixtures were calculated using equation (A):

$$V_m^E/(\mathrm{cm^3 mol^{-1}}) = (x_l M_1 + x_2 M_2)/\rho_m - x_l M_1/\rho_1 - x_2 M_2/\rho_2 \qquad \text{(A)}$$

where M_1 and M_2 represent the molecular weights of components 1 and 2 respectively. The x_1 and x_2 are the mole fractions of 1 and 2 components having densities ρ_1 and ρ_2, respectively. The density (ρ_m) is the experimentally observed density of the binary liquid mixtures. All measurements were carried out in a thermostatically controlled and well-stirred water-bath with a temperature accuracy of ± 0.01°C, read on a Beckmann thermometer.

RESULTS

The values of V_m^E were determined for the liquid mixtures: x *n*-butanol $+ (1-x_1)$ nitrobenzene, or $x + (1-x_1)$ aniline, or $x + (1-x_1)$ acetonitrile at temperatures of 298.15, 303.15, 308.15, and 313.15 K. The results are presented in Table II. The obtained V_m^E values

TABLE I Composition of density data (g cm^{-3}) between experimental and literature values at 298.15 K

n-Butanol		*Nitrobenzene*		*Aniline*		*Acetonitrile*	
Experimental	*Literature*	*Experimental*	*Literature*	*Experimental*	*Literature*	*Experimental*	*Literature*
0.8058	0.8060	1.2035	1.2037[a]	1.0175	1.0175	0.7766	0.7766

[a] Represents density data at 20°C.

TABLE II Excess molar volumes (V_m^E) of *n*-butanol with nitrobenzene–aniline–acetonitrile at different temperatures

Mole Fraction	*Temperature* (K)			
	298.15	*303.15*	*308.15*	*313.15*
System: *n*-butanol + (1−x_1) nitrobenzene				
0.1005	−0.2185	−0.2651	−0.3064	−0.3562
0.2008	−0.4008	−0.4325	−0.4759	−0.5382
0.3005	−0.5253	−0.5405	−0.5715	−0.6350
0.4006	−0.588	−0.6220	−0.6545	−0.7173
0.5001	−0.6275	−0.6614	−0.6987	−0.7578
0.6007	−0.6121	−0.6545	−0.6808	−0.7412
0.7009	−0.5719	−0.6224	−0.6499	−0.7027
0.8001	−0.4906	−0.5488	−0.5792	−0.6285
0.9001	−0.3179	−0.4031	−0.4273	−0.4796
A_0	−2.4855	−2.5873	−2.7008	−2.9287
A_1	−0.1761	−0.3009	−0.2869	−0.2050
A_2	0.7897	−1.4813	−1.8095	−2.2268
A_3	−0.8150	−0.9893	−0.8358	−0.9520
SD	±0.0045	±0.0153	±0.02073	±0.0265
System: *n*-butanol + (1−x_1) aniline				
0.1007	−0.1172	−0.1481	−0.1612	−0.1793
0.2003	−0.2063	−0.2421	−0.2775	−0.2878
0.3007	−0.3040	−0.3335	−0.3540	−0.3719
0.3998	−0.3782	−0.3789	−0.3899	−0.3959
0.5007	−0.3702	−0.3962	−0.4069	−0.4199
0.6006	−0.3493	−0.3706	−0.3821	−0.3899
0.7007	−0.2983	−0.3481	−0.3553	−0.3682
0.7998	−0.2113	−0.2552	−0.2664	−0.2923
0.8999	−0.1250	−0.1549	−0.1678	−0.1885
A_0	−1.4594	−1.5224	−1.6793	−1.7565
A_1	−0.0052	−0.0440	0.0232	0.0551
A_2	0.2918	0.0136	−0.1660	−0.4610
A_3	−0.0631	0.07940	0.0212	0.0287
SD	±0.0087	±0.01193	±0.00878	±0.0088
System: *n*-butanol + (1−x_1) acetonitrile				
0.1004	−0.1029	−0.1158	−0.1261	−0.1485
0.2001	−0.1760	−0.1996	−0.2263	−0.2493
0.3002	−0.2394	−0.2789	−0.3148	−0.3382
0.3999	−0.2854	−0.3373	−0.3569	−0.3711
0.4999	−0.3022	−0.3525	−0.3737	−0.3962
0.6005	−0.2891	−0.3399	−0.3656	−0.3870
0.7002	−0.2506	−0.2948	−0.318	−0.3482
0.8010	−0.1969	−0.2247	−0.2395	−0.2789
0.8999	−0.1166	−0.1257	−0.1673	−0.1789
A_0	−1.1929	−1.4101	−1.5059	−1.6449
A_1	−0.0592	−0.1088	0.1144	−0.1418
A_2	0.0394	0.2049	−0.1333	−0.3348
A_3	−0.0850	0.0560	−0.8048	0.3078
SD	±0.00482	±0.00501	±0.01938	±0.02256

were fitted with least square method to four parameters of Redlich and Kister [21] equation (B);

$$V_m^E/(\mathrm{cm^3 mol^{-1}}) = x_1(1 - x_1)\sum_{j=0}^{3}(A_j(2x_1 - 1)^j) \tag{B}$$

The values of A_j obtained by a least square method are summarized in Table II.

DISCUSSION

A relationship between the excess molar volumes and the mole fraction of *n*-butanol has been determined for each constituent such as nitrobenzene, aniline, and acetonitrile mixture at temperatures of 298.15, 303.15, 308.15, and 313.15 K. The results are shown in Figs. 1–3 and similar graphical features can be seen at investigated temperatures with chosen component mixtures. That is, a negative slope is followed by a positive after a particular mole fraction of *n*-butanol. In Fig. 1, the V_m^E of *n*-butanol and nitrobenzene mixture decreases with increasing the concentration of *n*-butanol. When a mole fraction of *n*-butanol was reached at 0.5001, the V_m^E values become lowest in all temperatures. The lowest values were found to be determined as −0.6275, −0.6614, −0.6987,

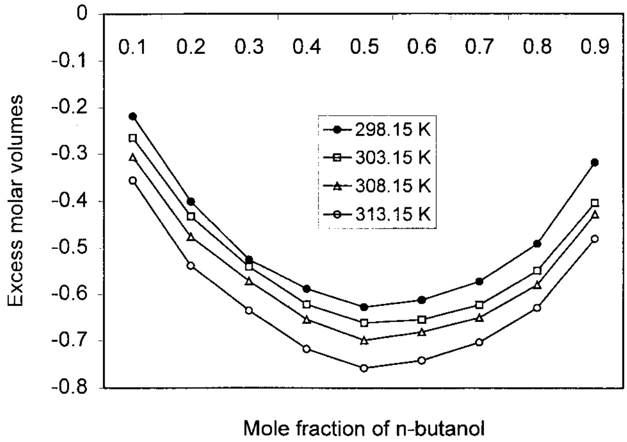


FIGURE 1 Effect of composition of mixture: *n*-butanol and nitrobenzene on excess molar volumes (V_m^E) at temperatures of 298.15, 303.15, 308.15, and 313.15 K.

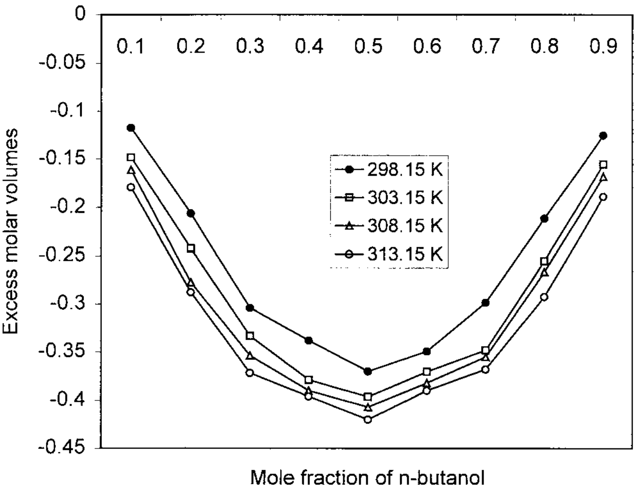


FIGURE 2 Effect of composition of mixture: *n*-butanol and aniline on excess molar volumes (V_m^E) at temperatures of 298.15, 303.15, 308.15, and 313.15 K.

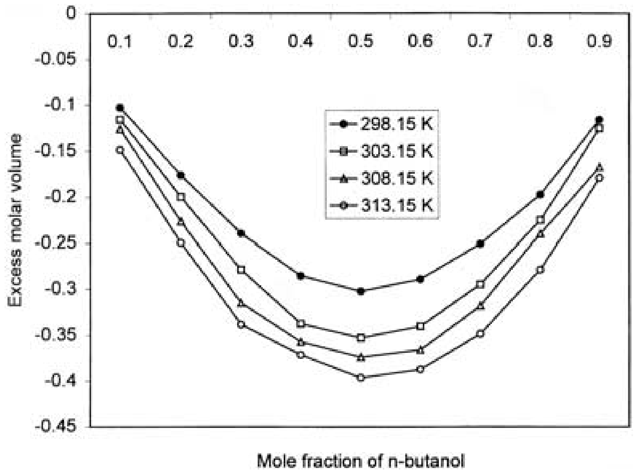
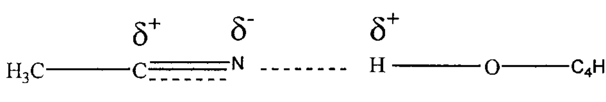


FIGURE 3 Effect of composition of mixture: *n*-butanol and acetonitrile on excess molar volumes (V_m^E) at temperatures of 298.15, 303.15, 308.15, and 313.15 K.

−0.7578 cm^3/mol at 298.15, 303.15, 308.15, and 313.15 K, respectively. An increment of the V_m^E was observed when the concentration of *n*-butanol was increased in the mixture and exceeded the minimum value. It was a common feature for all temperatures used. A similar result was observed for the *n*-butanol and aniline, and acetonitrile liquid mixtures (Figs. 2 and 3). The values of V_m^E decrease with increasing the mole fraction of *n*-butanol. The lowest values of V_m^E were found at 0.5007 and 0.4999-mole fraction when the aniline and acetronitrile were used, respectively. However, the lowest values of V_m^E, in the *n*-butanol and aniline system, were determined as −0.3702, −0.3962, −0.4069, and −0.4199 cm^3/mol at 298.15, 303.15, 308.15, and 313.15 K, respectively. For the *n*-butanol and acetonitrile mixture, the minimum V_m^E values were −0.3022, −0.3525, −0.3737 and −0.3962 cm^3/mol at 298.15, 303.15, 308.15, and 313.15 K, respectively.

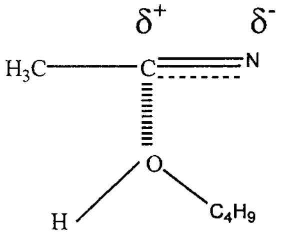
According to Fort and Moore [22], a negative excess volume is an indication of strong heteromolecular interaction in the liquid mixtures and is attributed to charge-transfer, dipole–dipole, dipole-induced-dipole interactions and hydrogen bonding between the unlike components, while a positive sign indicates a weak interaction and is attributed to depersive force (London forces), which are likely to be operative in every cases. The magnitudes of the contributions made by the different types of interactions will vary with the components and composition of the mixtures. In the present investigation, however, all the three mixtures gave negative magnitude of V_m^E, consistent with the presence of heteromolecular interaction in all the binary liquid mixtures, as indicated by the Fort and Moore observation.

Considering the *n*-butanol and acetonitrile mixture, it is probable that the interaction existing in the mixture is due to the formation of intermolecular hydrogen bonding between the cyano group (–CN) of acetonitrile and the hydroxyl group (–OH) of *n*-butanol. The hydrogen bonding interaction in the *n*-butanol with acetonitrile is as shown below:



$$H_3C — \overset{\delta^+}{C} \equiv \overset{\delta^-}{N} \cdots\cdots \overset{\delta^+}{H} — O — C_4H_9$$

It is probable that there is a dipole–dipole interaction in the *n*-butanol between the carbon atom of cyano group and the oxygen atom of hydroxyl group as shown below;



The dipole moments of the investigated *n*-butanol, nitrobenzene, aniline, and acetonitrile constituents are 1.63, 3.90, 1.53, and 3.0, respectively. Overall, the V_m^E (Figs. 1–3) for *n*-butanol and nitrobenzene, *n*-butanol and aniline, and *n*-butanol and acetonitrile mixtures can be explained in terms of (i) dipole–dipole interaction between the polar components and (ii) steric effect. The negative values of V_m^E of *n*-butanol + nitrobenzene and *n*-butanol + acetonitrile (Figs. 1 and 3) may be attributed to the breaking of self association existing in the pure liquids and the formation of hetero-association among the molecules of binary mixtures, where the latter is predominant. The partial accommodation of linear *n*-butanol molecule in between the interstitial spaces of the cyclic nitrobenzene and *n*-butanol + acetonitrile mixtures of specific interaction due to high polarity of the second components results in the decrease of the molar volumes of the mixtures. The excess molar volumes *versus* mole fraction of *n*-butanol curves (Figs. 1 and 3) showed a general agreement of shape with reported works for different mixtures such as butanol and benzene [23], toluene and aniline, water and aniline, *n*-hexane and aniline [11], and toluene and acetonitrile, and toluene and nitrobenzene [16]. In Fig. 2, the dipole moments of the components molecules are not very different, and the specific interaction between the unlike molecules are not unexpected. However, partial accommodation of the *n*-butanol molecule in between the aniline molecule may lead to decrease in the molar volume of the mixtures. It is also a fact for all mixtures that the creation of order would produce the negative V_m^E values. This interpretation can be applied to all the mixtures investigated in this study. The negative V_m^E values displayed by all the mixtures indicate a more ordered structure in solution. The negative values showed by all the mixtures were increased as the temperature increased. It suggests that interaction of components of solution was increased with increasing the temperatures.

CONCLUSIONS

The V_m^E from the densities data have been evaluated for binary mixtures of *n*-butanol with nitrobenzene, aniline, acetonitrile at four temperatures; 298.15, 303.15, 308.15, and 313.15 K. Analyses suggest the presence of a strong intermolecular interaction in all binary mixtures, which may be due to the dipole–dipole interaction between polar components, steric effects, and specific interaction between unlike molecules. The strength of intermolecular interaction increases with rise in temperatures.

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