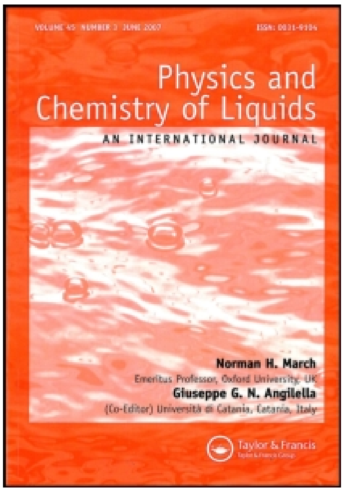

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Molar Excess Volumes of Ternary Mixtures of Non-Electrolyte Solutions at 303.15 K

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To cite this Article Sastry, G. Subramanya , Srinivasulu, U. , Sivakumar, K. and Naidu, P. Ramachandra(1994) 'Molar Excess Volumes of Ternary Mixtures of Non-Electrolyte Solutions at 303.15 K', Physics and Chemistry of Liquids, 28: 1, 35 — 40

To link to this Article: DOI: 10.1080/00319109408029538

URL: http://dx.doi.org/10.1080/00319109408029538

Phys. Chem. Liq., 1994, Vol. 28, pp. 35–40
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MOLAR EXCESS VOLUMES OF TERNARY MIXTURES OF NON-ELECTROLYTE SOLUTIONS AT 303.15 K

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(Received 15 September 1993)

New excess volume data for four ternary mixtures were measured at 303.15 K. The mixtures included di-n-butylamine and n-heptane as common components. The non-common components were 1-pentanol, 1-hexanol, 1-heptanol and 1-octanol. Excess volumes are negative over the entire range of composition in the four mixtures. The experimental data were compared with those predicted by empirical equations.

KEY WORDS: Excess Volume, mole fraction, empirical equations

INTRODUCTION

The measurement of thermodynamic properties of ternary and multi-component mixtures become difficult as these involve sophisticated instruments and the complex problems associated with the operation of the units. Hence attempts[1–7] have been made to predict thermodynamic data from the experimental data of constituent binaries using empirical and semi-empirical equations. Most of these equations take into account mainly pair-wise interactions. However, recently Hwang *et al.*[8] have proposed a semiempirical equation which take into account both two body and three body interactions. It has been shown that the expression satisfactorily estimates ternary free-energies of some aqueous-organic systems. The equation has been ex tended to excess volumes of ternary mixtures by Acree and Naidu[9]. These workers observed that the equation predicts excess volumes and favourably compared with Redlich–Kister equation. We report here the new ternary excess volume data for four ternary mixtures and the data are compared with those predicted by the expressions of Hwang *et al.* and Redlich–Kister.

EXPERIMENTAL PROCEDURE

Excess volume data for ternary systems were measured with the three-limbed dilatometer described by Naidu and Naidu[10]. The dilatometer contained three bulbs

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of different capacities. Mercury was used in the bottom to separate the components. One of the three bulbs was fitted with a capillary, and the other two were fitted with ground glass stoppers. Four dilatometers of the aforesaid type were used to cover the entire range of composition. All the measurements were made at constant temperature employing a thermostat that could be maintained to ±0.01 K. The measured V^E values were accurate to $\pm 0.003\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$.

All the chemicals used were of analytical grade. Di-n-butylamine (BDH Poole, England) was used without purification. 1-Pentanol (BDH), 1-hexanol (BDH), 1-heptanol (Koch-light laboratories limited, England), 1-octanol (SISCO) and n-heptane (S. D. Fine Chemicals) were purified by the methods described in the literature (11). The purity of the sample was checked by comparing the measured density of the compounds with those reported in the literature (11, 12). Densities were determined with a bicapillary type pycnometer, which offers an accuracy of 2 parts in 10^5. The measured densities and those reported is the literature are given in Table I.

RESULTS AND DISCUSSION

The dependence of V^E on composition may be expressed by an empirical equation proposed by Redlich–Kister (1) as follows

$$V^{E(12)} = X_1 X_2 [a_0 + a_1 (X_1 - X_2) + a_2 (X_1 - X_2)^2] \quad (1)$$

Hawng *et al.* (8) developed the relation

$$A^{E(12)} = G^{E(12)} = X_1 X_2 [A_0 + A_1 X_1^3 + A_2 X_2^3] \quad (2)$$

for binary mixtures taking into account two body and three body interactions. Acree and Naidu (9) adopted the equation for excess volume in the following form

$$V^{E(12)} = X_1 X_2 [V_0 + V_1 X_1^3 + V_2 X_2^3] \quad (3)$$

Table I Densities (ρ) of pure components at 303.15 K.

	$\rho(\mathrm{g\,cm^{-3}})$	
Components	*Literature* (11, 12)	*Present Study*
di-n-butylamine	–	0.75519
1-pentanol	0.80764	0.80769
1-hexenol	0.81201	0.81209
1-heptanol	0.81574	0.81571
1-octanol	0.82192	0.82188
n-heptane	0.67538	0.67530

and these workers also extended the predictive approach to ternary V^E and employed the equation

$$\begin{aligned} V^{E(123)} &= X_1 X_2 [(V_0^{(12)} + V_1^{(12)} X_1^3 + V_2^{(12)} X_2^3)] \\ &+ X_1 X_3 [(V_0^{(13)} + V_1^{(13)} X_1^3 + V_3^{(13)} X_3^3)] \\ &+ X_2 X_3 [(V_0^{(23)} + V_2^{(23)} X_2^3 + V_3^{(23)} X_3^3)] \end{aligned} \tag{4}$$

to predict the ternary V^E data from the basis of constituent binaries. The predicted data were compared with experimental results of some ternary mixtures and concluded that the new predictive expression gives a good estimate of ternary V^E.

We analyse here new experimental V^E data for four ternary mixtures in the light of aforesaid equations. Binary V^E parameters for di-n-butylamine with 1-pentanol, 1-hexanol and 1-heptanol and heptane with 1-alcohols were taken from the literature (13, 10). Further, the binary V^E parameters for the systems di-n-butylamine with 1-octanol and with n-heptane were also computed from the measured V^E data in the present investigation and these are graphically presented in Figures 1 and 2. All the

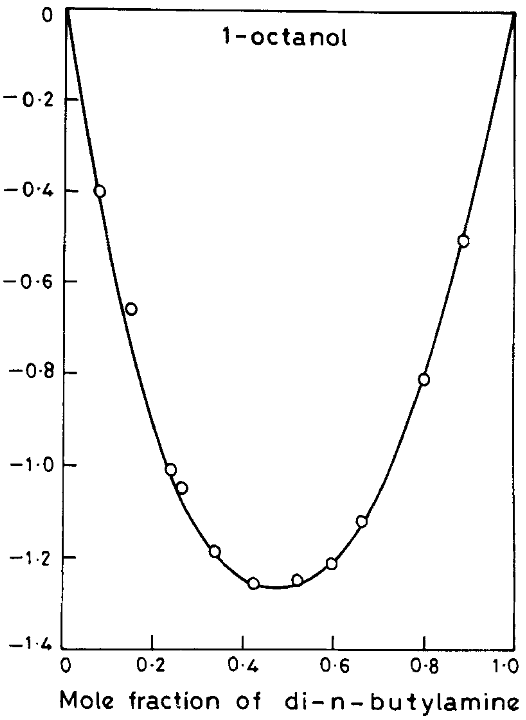

Figure 1 Excess molar volumes V^E at 303.15 K plotted against mole fraction X_1 for di-n-butylamine (1) + 1-octanol (2).

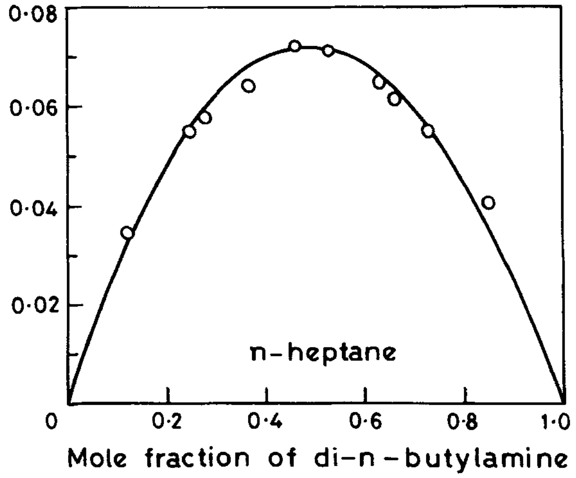

Figure 2 Excess molar volumes V^E at 303.15 K plotted against mole fraction X_1 for di-n-butyl-amine (1) + n-heptane (2).

above binary parameters are computed using Redlich–Kister relation and are listed as Table II. The 'V' coefficients in the equation (4) were computed from the smoothed binary experimental data at mole fraction $X_1 = 0.2, 0.5$ and 0.8. The values of 'V' coefficients are given in Table III.

The measured excess volume data, and those of computed from the relations proposed by Redlich–Kister and Hwang *et al.*, are given in columns 3, 4 & 5 of

Table II The binary parameters obtained by the method of least squares using Redlich–Kister equation

System	a_0	a_1	a_2
di-n-butylamine (1) + 1-pentanol (2) + n-heptane (3)			
di-n-butylamine (1) + 1-pentanol (2)	−4.751	0.144	0.684
di-n-butylamine (1) + n-heptane (3)	0.273	−0.002	0.089
1-pentanol (2) + n-heptane (3)	0.408	−1.104	0.071
di-n-butylamine (1) + 1-hexanol (2) + n-heptane (3)			
di-n-butylamine (1) + 1-hexanol (2)	−5.020	−0.133	0.652
di-n-butylamine (1) + n-heptane (3)	0.273	−0.002	0.089
1-hexanol (2) + n-heptane (3)	−0.140	−0.644	0.145
di-n-butylamine (1) + 1-heptanol (2) + n-heptane (3)			
di-n-butylamine (1) + 1-heptanol (2)	−5.347	0.884	−0.252
di-n-butylamine (1) + n-heptane (3)	0.273	−0.002	0.089
1-heptanol (2) + n-heptane (3)	0.587	−0.758	−0.881
di-n-butylamine (1) + 1-octanol (2) + n-heptane (3)			
di-n-butylamine (1) + 1-octanol (2)	−5.216	0.382	−0.051
di-n-butylamine (1) + n-heptane (3)	0.273	−0.002	0.089
1-octanol (2) n-heptane (3)	−0.969	−0.285	−0.592

Table III The binary parameters obtained by using Hwang *et al.*, Eq. (3).

System	$v_0^{(ij)}$	$v_1^{(ij)}$	$v_2^{(ij)}$
di-n-butylamine (1) + 1-pentanol (2) + n-heptane (3)			
di-n-butylamine (1) + 1-pentanol (2)	−4.979	1.083	0.740
di-n-butylamine (1) + n-heptane (3)	0.244	−0.115	0.121
1-pentanol (2) + n-heptane (3)	0.385	−1.220	1.408
di-n-butylamine (1) + 1-hexanol (2) + n-heptane (3)			
di-n-butylamine (1) + 1-hexanol (2)	−5.237	0.708	1.025
di-n-butylamine (1) + n-heptane (3)	0.244	0.115	0.121
1-hexanol (2) + n-heptane (3)	−0.188	−0.576	0.960
di-n-butylamine (1) + 1-heptanol (2) + n-heptane (3)			
di-n-butylamine (1) + 1-heptanol (2)	−5.263	0.716	−1.388
di-n-butylamine (1) + n-heptane (3)	0.244	0.115	0.121
1-heptanol (2) + n-heptane (3)	−0.294	−2.077	−0.273
di-n-butylamine (1) + 1-octanol (2) + n-heptane (3)			
di-n-butylamine (1) + 1-octanol (2)	−5.199	0.388	−0.523
di-n-butylamine (1) + n-heptane (3)	0.244	0.115	0.121
1-octanol + (2) + n-heptane (3)	−0.772	−1.128	−0.450

Table IV Experimental and predicted excess molar volumes for the ternary mixtures of di-n-butylamine (1) + 1-alcohol (2) + n-heptane (3) at 303.15 K.

Mole fraction of di-n-butylamine X_1	*Mole fraction of an alcohol* X_2	$V^{E(123)}$exp	$V^{E(123)}$ *Redlich–Kister*	$V^{E(123)}$ *Hwang et al.*	${}^{a}\Delta V^{E(123)}$ *Redlich–Kister*	${}^{b}\Delta V^{E(123)}$ *Hwang et al.*
di-n-butylamine (1) + 1-pentanol (2) + n-heptane (3)						
0.0713	0.8687	−0.414	−0.296	−0.299	−0.118	−0.115
0.1245	0.8230	−0.617	−0.478	−0.479	−0.139	−0.138
0.1796	0.7004	−0.960	−0.596	−0.589	−0.364	−0.371
0.3039	0.5888	−1.184	−0.838	−0.841	−0.346	−0.343
0.3748	0.5131	−1.254	−0.904	−0.904	−0.350	−0.350
0.5075	0.3573	−1.386	−0.827	−0.832	−0.559	−0.554
0.5739	0.3387	−1.187	−0.891	−0.899	−0.296	−0.288
0.6589	0.2819	−1.023	−0.829	−0.847	−0.184	−0.176
0.7476	0.1620	−0.863	−0.512	−0.522	−0.351	−0.341
di-n-butylamine (1) + 1-hexanol (2) + n-heptane (3)						
0.0697	0.8511	−0.371	−0.303	−0.308	−0.068	−0.063
0.1497	0.8003	−0.660	−0.579	−0.581	−0.081	−0.079
0.1649	0.7321	−0.776	−0.604	−0.610	−0.172	−0.166
0.2838	0.6369	−1.100	−0.901	−0.907	−0.199	−0.193
0.3707	0.5267	−1.280	−1.005	−0.992	−0.275	−0.288
0.5197	0.3751	−1.260	−0.974	−0.986	−0.286	−0.274
0.5919	0.2752	−1.097	−0.799	−0.812	−0.298	−0.285
0.6543	0.2358	−0.986	−0.750	−0.800	−0.236	−0.186
0.8015	0.1129	−0.518	−0.414	−0.422	−0.104	−0.096

Table IV (*Continued*)

Mole fraction of di-n-butylamine X_1	*Mole fraction of an alcohol* X_2	$V^{E(123)}$exp	$V^{E(123)}$ *Redlich–Kister*	$V^{E(123)}$ *Hwang et al.*	$^{a}\Delta V^{E(123)}$ *Redlich–Kister*	$^{b}\Delta c^{E(123)}$ *Hwang et al.*
		di-n-butylamine (1) + 1-heptanol (2) + n-heptane (3)				
0.0979	0.8223	−0.633	−0.598	−0.579	−0.035	−0.054
0.1648	0.7621	−0.913	−0.831	−0.803	−0.082	−0.110
0.2458	0.5568	−1.051	−0.867	−0.811	−0.184	−0.240
0.3497	0.4666	−1.175	−0.947	−0.904	−0.228	−0.271
0.3784	0.4222	−1.113	−0.894	−0.871	−0.219	−0.242
0.4817	0.3306	−1.031	−0.850	−0.834	−0.181	−0.197
0.6888	0.2129	−0.822	−0.727	−0.726	−0.095	−0.096
0.7075	0.2320	−0.900	−0.815	−0.803	−0.085	−0.097
0.7711	0.1423	−0.559	−0.524	−0.542	−0.034	−0.017
		di-n-butylamine (1) + 1-octanol (2) + n-heptane (3)				
0.0958	0.8035	−0.568	−0.539	−0.529	−0.029	−0.039
0.1749	0.7665	−0.862	−0.795	−0.784	−0.067	−0.078
0.2000	0.6840	−0.973	−0.839	−0.818	−0.134	−0.155
0.3326	0.5602	−1.285	−1.052	−1.032	−0.233	−0.253
0.4273	0.4595	−1.323	−1.072	−1.059	−0.251	−0.264
0.5275	0.4058	−1.333	−1.128	−1.122	−0.205	−0.211
0.6571	0.2525	−0.973	−0.847	−0.848	−0.126	−0.125
0.6830	0.2197	−0.840	−0.760	−0.761	−0.080	−0.079
0.7914	0.1332	−0.523	−0.517	−0.518	−0.006	−0.005

[a] $\Delta V^{E(123)} = V^{E(123)}$exp − $V^{E(123)}$Redlich–Kister

[b] $\Delta V^{E(123)} = V^{E(123)}$exp − $V^{E(123)}$Hwang *et al.*

Table IV respectively. Also the difference between experimental data and that of calculated from Redlich–Kister and Hwang *et al.*, relation, ΔV^E_{123}, are given in columns 6 and 7 of Table IV.

An examination of experimental and predicted data, included in Table IV, suggest that both experimental and predicted data have the same sign. However, the difference between the sets of the data exceed the experimental error. Finally, the data shows that predictive capabilities of the expressions are similar.

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